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Analysis of catastrophic failure of poly (ethylene terephthalate) pressurized bottle

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Abstract

PET bottles use is widespread as it used to package a vast variety of materials, from beverage, food to house products we buy daily. PET, acronym for poly (ethylene terephthalate), is one of the most used thermoplastic polymer and offers a range of benefits as a material for bottle manufacture; it is light, clear, safe, and in particular offers high mechanical strength.

This is of particular interest to us since objective of this thesis is to propose a design for a small bottle that is capable of coping with internal pressure cycling. Manufacturing industry is not only looking at plastic bottles for solely purpose of storage but there is always interest for novel applications as part of equipment like a sprayer or even use to mix, dispense.

In this work we explore polymer properties, investigate analytical materials available to characterize proposed design and manufacture robustness, and derive recommendations from pressure vessel design to assist a bottle proposal and finally simulate in with ANSYS finite element software the critical geometry regions of the bottle base under proposed pressure cycling to validate overall performance.

Acknowledgments

I would like to express deep gratitude to my supervisor Prof Dr Michele Meo whom not only has guided me during the development of this thesis but has also strengthened my understanding in many complex engineering subjects of FEA simulations, application to mechanical design. I have also learned a lot from his student and post-doc group of department mechanical engineers, always available to offer support.

I would also like to thanks Dmitri Ginzburg in assisting during preliminary material properties definitions at the beginning of this master thesis and finally to the University of Bath as it has fully lived up to the expectations in terms of quality of student tuitions, support provided, progress management, learning opportunities, ready to help infrastructure and an excellent environment that welcomes not only full time students but also working students like myself that can only progress their studies part time.

Contents

Chapter 1

Introduction

1.0 Packaging background

It is only relatively recently in the human social history that we have learned the importance of preserving food safety and quality by encasing it in a protective cover after processing. Among the first records in 1908, public health officer in Kansas, Dr Samuel J. Crumbine paid more attention in to a common practise in those days and noted how a young girl was drinking water from the same communion cup that had just been used by his tuberculosis patient [1]. Dr Crumbine kicked off a public health complain and packaging science was born. To most consumers packaging is a shell, a container unworthy of second thoughts but as a technological device its vital functions are numerous. Depending on the application, for example, it has to be strong in spite of the thin walls, must be light but retain some rigidity, it has to stop moisture migration, protect from biohazards, must be recyclable, and prevent cross contamination as it comes into contact with other foods during the long journey to the consumer. It must also prevent label glue and other print chemical (even gases) to reach the product and finally be affordable with lowest impact on final overall product cost. A rightful modern environmentally conscious awareness is challenging the uncontrolled global use of plastic, for example oceans are now clearly polluted with ubiquitous packaging waste and marine life is often fatally affected. But while the global waste crisis must be resolved preserving human health must be also guaranteed and such a balance will be very difficult to establish.

One further significant demand has been laid upon this technology, a demand that is harsh in strength and time; it must resist to gas pressure and remain safe for indefinite time. This is of particular interest to this thesis that aims at delivering a safer bottle base design for a novel industrial application of a PET container that will be subjected to limited cycle pressure during use.

Vat breweries had been producing gas for a good ten thousand years but it was in 1772 that while Joseph Priestley was experimenting with such gases that he demonstrated that a drink could be carbonated [2].

The birth of carbonated drink industry brought the need for pressure resistance since such carbonated drink can easily challenge their containers with a pressure that can exceed 3 bar especially as storage temperature rises. Such pressure confined within the significant bottle volume poses a significant risk to people in the case of bottle burst. Gas pressure within these containers can be considered relatively constant even if some changes can be expected during transport shaking and storage as temperature fluctuates. When robustness is required the material choice falls quickly on PET. PET, Polyethylene terephthalate, is a thermoplastic polymer, has been around for 60 years and its demand has been in steadily growth over the past couple of decades in line with specific producers growth like for the carbonated drink industry . PET has high strength, high dimensional stability, broad temperature range, crystal clarity, easy to print on, good solvent resistance and offers barrier not only to water vapour but also to oxygen [3]. One of the reason of such a success is that PET has a strong ability to crystallize at the temperature and strain rates that happens during deformations imposed by the manufacturing process [4].

1.1 Motivation and Objectives

Plastic bottles are a familiar packaging format produced to deliver drinks that are carbonated or un-carbonated to the consumer. PET bottles destined to the carbonated industry are commonly manufactured with stretch blow moulding process starting from PET pellets delivered from the supplier. The produced bottles are then stacked and stored before delivering to the filling site that is chosen conveniently as close as possible to minimise transportation cost; in fact in big filling operations blow moulding is located within the filling factory.

Objective of this work is to propose a plastic bottle design for a novel application capable of coping with pressure stresses result from injecting fluids in a bottom connector for a potentially novel industrial application. Since the critical weakness occurs in the bottle base both the connector in the and the neck docking system are not part of this work as these will be evaluated in the future together with other more generic packaging tests like for example, top loading strength, bottle deformations during transportations, capping performance. Generally bottles can be thought as passive dispenser, in the way that consumer pour the content taking advantage of gravity but this can only be accomplished when the fluid-dynamical properties of the sold product fall within a favourable range at

the user temperature. Example of these products are coke, orange juice and other water based fluids but there are many other materials (food and non-food) as long as their viscosity is low enough to allow for gravity pour. The design brief indicated a bulk bottle base diameter, specified PET as material, preference for a non-hemispheric base as potential use of the embodiment might be upright store position therefore a base with feet design would spare the use of a base cap with material cost, assembly and environmental impact mitigation. Pressure is to be applied via an air pressure connector located in the centre of the base. It is envisaged that the connector is more likely to be manufactured separately and only later attached permanently to the bottle preform by various means, though spin welding is a possible robust possibility. The assembled preform-connector can then be stretch blow moulded in the final bottle. Objective of the study is to suggest possible base designs and relative analytical evaluations, foreseeing manufacturing issues and issues mitigation, analytical technique to validate a manufactured prototype. Apologies if some of the information is not available but this work is part of a potential novel application and some of the detail could not be clearly disclosed. Another limitation to remember is that the experimental observations are based on pilot scale limited expensive production and therefore findings confirmation will follow in future work.

1.2 Thesis Outline

Chapter 2 explores the literature review starting from polymers generally used in packaging, why PET is a good material for bottles that will be subjected to internal pressure during service, preform making and bottle blowing at converters.

Pressurised vessel theory is also reviewed, a lot of papers deal with metal tanks for construction and chemical industry but nevertheless previous work in this area should be consulted.

Second part of Chapter 2 then looks at a variety of tests available to evaluate and diagnosticate PET bottles issues.

Chapter 3 reports of the tests carried out on a small pilot scale test using the main bottle design.

Chapter 4 looks at FEA analysis of the propose design and investigates the mechanical performance of the chosen geometry with the relevant thickness.

In Chapter 5 the final discussion with recommendations.

Chapter 2

Literature review and tests

2.0 Packaging polymers

Plastic comes in a vast variety of properties, easy of manufacturing and affordable costs and for these reasons are integral part of human everyday life and can be found in most disparate applications; from medical to foods, in home, office, automobile etc.

Plastic is a desirable material because its properties can be accurately tailored to meet the application by controlling: - molecular weight, molecular weight distribution, chain interactions, degree of crystallisation, side chain length, amount of orientation during manufacturing process, copolymerization, addition of compounds like for example plasticizers, stabilisers.

Plastic materials took their major leap in these recent decades but first natural forms were known even six centuries ago; rubber and later it was discovered that the addition of sulphur produce a steep improvement on the material properties. For a long time researchers incorrectly thought they were colloids; these are more generally a mixture of dispersed insoluble particles that are suspended in another substance. Sometime the dispersed insoluble particles without the suspending substance are called colloids. The particle range distribution of the dispersed phase range from 1 to 1000 nanometres [12].

In 1920 when H. Staudinger finally recognized them as macromolecules, that is very large molecules (like proteins), within the decade Carothers produced nylon (polyesters and polyamides) and Ziegler-Natta's anionic catalyst work allowed the introduction of polyethylene, high density linear polyethylene, species of stereo-specific polymers.

The term polymer (from the Greek many parts) indicates giant molecules made up by polymerizing smaller molecules called monomers, that have unique properties; they are tough, viscoelastic, tend to form glasses and semi crystalline structures. Examples are proteins, DNA, form of biopolymers and plastics and rubber that are examples of synthetic polymers. The latter two, of interest in our application, can be separated by looking at the glass transition temperature (Tg, a fundamental property where a polymer state changes from a hard-glassy material to a soft rubbery obtained from

studying the change of elastic modulus versus temperature). In plastics the glass transition temperature is above room temperature for rubbers, Tg, is lower than room temperature.

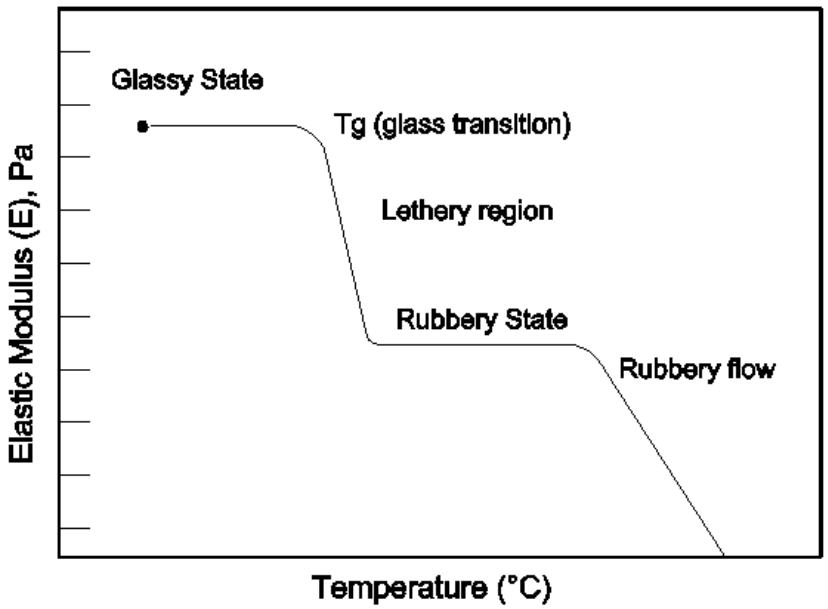


Figure 1-0: Material elastic modulus variation versus temperature

At low temperature the material follows closely hooks law $\sigma = \mathrm{E}\varepsilon$, where stress strain are bound the young modulus E. A leathery region follows where the young modulus drops three fold and then a rubbery plateau region.

An important differentiation that can be made observing if the polymer branches cross-link is between thermoplastic (like PET) and thermoset plastic materials. As we were discussing plastic materials are made polymers that can exist spatially more or less linearly distributed (amorphous versus more compacted semi-crystalline) but never cross-linked (thermoplastic) or they can form covalent bonds between the chains. Intra-chain interaction is also very important in affecting the mechanical properties of polymers. The degree of crosslinking can expressed mathematically by referring to the diamond structure. In a diamond the carbon in the parallel carbon chains links with a maximum number of crosslinking possible therefore we can define as the density of crosslinking density as 1. Thermoset polymers can have a crosslinking value of 10^{-1}.

An important characteristic of thermoplastic materials is that differently from thermosets where the branches have strong repetitive inter-branch bonds, thermoplastic materials can be reprocessed with heat and re-shaping equipment. While it is possible that the long chain of polymers can align it is

more probable that due to their size the long molecules twist when the fluid cools therefore unlikely metals, for example, that can be completely crystallized, polymers tend to be in a partially, if not complete amorphous state [13].

Polymers can also be made by two different type of low molecular weight species, these macromolecules are called copolymers as for example ethylene vinyl acetate which is a copolymer of ethylene and ethylene vinyl acetate. Of great interest to us is the mechanical strength of polymers and this might vary over a wide range, $1\ \mathrm{MN}/m^2$ to $50\ \mathrm{GN}/m^2$by controlling the material microstructure and manufacturing process. In its simple form a polymer can assume an amorphous state. In this state the polymer structure is completely randomly unordered, for example polystyrene. As the material assumes a more ordered form it packs more tightly and this is the semi-crystalline state like polypropylene. If the backbone structure making up the material allows then further packing is possible and full crystalline state can be reached.

A general for of a polymer material stress strain relationship is illustrated in figure 2

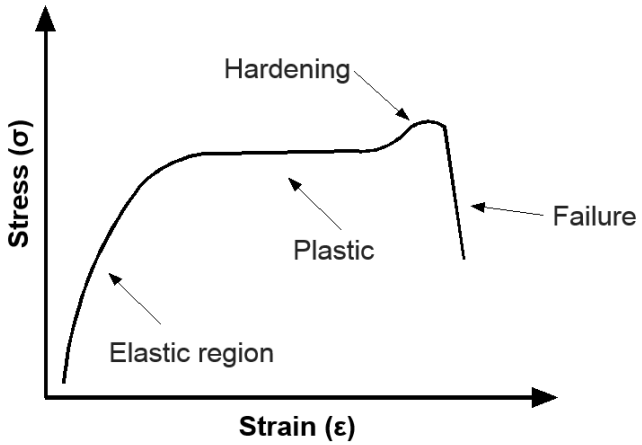


Figure 2: General polymer material stress strain relationship

Thermoplastic materials in amorphous state experience a low glass transition temperature in comparison to other materials therefore they also show a lower young modulus (E) and in addition as the temperature increases beyond the glass transition temperature even small increases of temperature increase the chance of chains slipping over one another therefore causing the young modulus to drop faster in this region. When crystalline regions start appearing and thermoplastic materials enter a semi-crystalline state the young modulus increases and as semi-crystalline regions

remain elastic longer than the amorphous regions so is the behaviour of the overall material. When strain goes beyond the elastic limit the polymer chains have slid for such a long distance the non-recoverable plastic deformation set in. Such deformation can be accompanied by crazing; as stresses overcome the weak van der Waals forces a micro-gap forms as the stronger covalent bond stretch following van der Waals bond failure [14]. To be noted that a craze behaviour is opposite to a crack as it can support the load, in-fact crazed regions show a higher energy absorption per unit of surface when compared with regions that were craze free even though inter-crazed crazed regions are often under considerable stress. Microfilaments, can be thought as rod like structures, called fibrils stretch along and support these micro-gaps. In semi-crystalline amorphous state the plastic deformation sets in first in the amorphous region that stretch first and then to crystalline region.

2.1 PET – poly (ethylene terephthalate) polymer

PET can be synthesized by an interchange process starting from dimethyl terephthalate and ethylene glycol. The process start with a temperature of ca. 175 C and involves methanol distillation, this is followed by an increase temperature stage to almost 300C (melt polymerization). During this second stage the ethylene glycol needs to be quickly removed to ensure high molecular weight product is achieved (average molecular weight, Mn of ca. 20,000 g/mole). The average molecular weight can only be increased to a certain limit, this because at these high temperatures molecule end groups decompose forming acetaldehyde. The final polymerization is also inhibited by thermal ester scission which again increases at such temperatures.

Crystallite orientation and amount of crystallisation have a direct effect on the resin mechanical properties. The density of PET is $1.333\ g/cm^3$ when in amorphous state and $1.455\ g/cm^3$ in crystal state respectively therefore one can determine the crystallized fraction by either measuring the density of the resin or by DSC (differential scanning calorimeter) analysis.

PET crystallisation is not a fast process and this is an issue in injection production as it impacts on production time and therefore costs. The use of plasticisers and nucleating agents can significantly improve the process but it is important to ensure that the injection process is in full controlled delivering the right material. As the word suggest these agents improving crystallization by offering as

point that initiate crystallisation. Nucleating agents are used in injection moulding, blow moulding, thermoforming at a varying levels, in the case of crystalline PET these levels are 1% and typical are added as powders or suspensions as long as there are good processing procedures that allow good dispersion. Nucleating agents also help clarity because they shift the crystal size distribution towards smaller size and as the crystals become smaller than the wavelength of the visible light it gets scattered at smaller angles therefore appearing less hazy and clearer. Typical nucleating agents are substituted sorbitols, low molecular weight polyolefins, sodium benzoate and ionomer resins.

2.2 PET bottle manufacturing making preform and blow moulding

2.2.1 Preforms.

PET pellets are dried (ca. 165°C) before that can be melted in the extruder and fed to the mold at pressure for injection. Drying is a very important process as if residual moisture is present beyond 50 ppm it will react with PET lower excessively the IV value (beyond 0.04 IV value) and mechanical performance will be suboptimal. Drying time and drier conditions should be tested within the particular preform making line so that the values of temperature and air flow distribution round the pellet achieve a consistent elimination of moisture from the batch. Coloured pellets can be used to measure the time it takes for them to appear in the preform.

The two injection moulds, female and male, close and the molten PET is injected through the gate which normally is central but in an application such as this where an air connector occupies the central position the designers are forced to locate the gate off centre. Normally the molten fluid will evenly flow in the cavity filling gradually the cavity from the gate towards the periphery but with an offset gate the flow fill preferentially start flowing off centre, following the off centre position of the gate and travel round the cavity to meet on the opposite side forming a longitudinal weld line. If process conditions are correct the welded line, normally visible should not affect the mechanical performance but if pressure performance is out of standard this is one of the check point to monitor. There are FEA simulation packages that specifically model the PET plastic flow in the cavity and they should be part of the developments if material joins poorly in the weld line and weaker spots can favour later crack initiation that might lead to a burst. We should just mention that even with centrally located gates it is

still be possible for the molten fluid to preferentially flow over one side this phenomena is called core shift and can lead to uneven wall thickness in the final preform.

As preform have a thicker wall than other injection molded products the injection pressure are not as high as in other form injections this is done ensure that the relative drag against the wall is minimised to avoid excessive shear. The PET freezes as it touches the cavity wall as these are cooled by water, a thin wall layer forms causing the relative channel to become narrower therefore when designing the cavity the wall thickness this should be wider to account for it. Gases are formed in the cavity and these must be efficiently evacuated via numerous vents as trapped gas or slow diffusing gasses causing sink marks. Good internal mold surface finish also reduces sink marks together with good pressure hold settings that compensate for material shrinkage by maintaining for a short time even pressure to feed the cooling dependant volume contraction. The molten material cooling eventually reaches also the gate area where the most recent fed PET, therefore hotter, is present. This can cause issues in this particular region as it should be part of studies if mechanical issue affect the bottle base.

2.2.2 **Preform molding**.

During blow moulding the preform is heated (95°C to 120°C) using infrared lamps (halogen lamps singularly voltage controlled using 0 to 99% parameter displayed on the blowing machine controller, peak wavelength 1200 nm) and stretched under pressure and with the aid of a pushing rod inserted through the neck, as the bottle forms the PET material assumes bi-axial orientation with a partially crystallized structure. The ratio of the final bottle length to the initial length is called stress ratio; during the preform stretch cycle within the mould a certain force has to be applied that depends by the blowing conditions but there is point during stretch where the force required suddenly increases, this point is called natural stretch ratio (NSR). The NSR point represents the transition between the yielding point and work hardening region in the PET stress-strain curve. After this point the material orientates with the applied stress and generally material mechanical performance improves (Tensile module of elasticity increases from 3170 Mpa to almost 5000 Mpa while at yield point the stress goes from 82 to 172 Mpa). NSR values are higher for low IV (intrinsic viscosity) PET has polymer chains can be stretched more compared to the high IV value. While a successful preform design will allow the PET material to orientate when the bottle touches the mould it is important to prevent

overstretching as this indicates that process has trespassed in the fracture region. In this stress-strain plot region numerous micro-cracks form in the bottle base giving the bottle a particular unpleasant white milking appearance known as pearlscense.

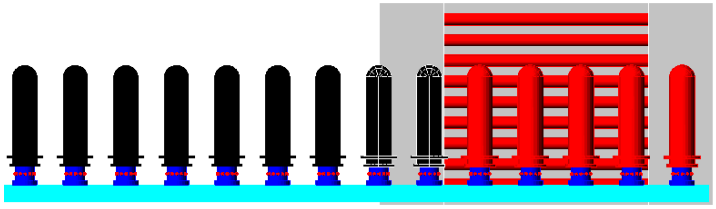


Figure 3: Infrared lamps heat the preforms (in red) before blowing stage downstream

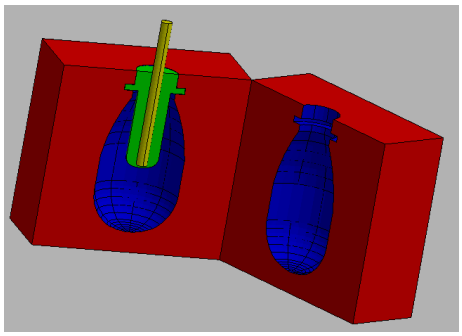


Figure 3-1: Stretch rod stretches the preform to fit the bottle mould

2.3 Pressure vessel basic theory

Typical pressure vessels have cylindrical, spherical, conical, toroid shapes though design complications can arise when, for example, nozzles or feeding ports are added for various flow exchange functions [20]. Plastic bottles that need to stand upright without adding a support attachment to the bottle base, tend to have some form of complex geometry that results in a series of valleys and troughs that complicate the stress-strain field generated on the wall as a result of the gas injected pressure. Stress analysis in mechanical engineering investigates how external forces that are applied to a structure relate to the corresponding stresses they generate. The separation study of design condition loadings and the effect, stresses, they produce helps deeper understanding and better design. When the ratio thickness is much smaller than the other dimensions, R (m/t>10), then

the pressure containers are referred as membranes and the load induced stresses as membrane stresses. These membrane stresses are assumed uniform and operate tangentially to the surface is consider to offer no resistance to bending. If the wall generates resistance when bending force are generated then bending stresses occur on top of the membrane stresses. The bottle in this study has a geometry much more complicated therefore membrane stress are insufficient to characterize the complete true stresses that arise from the pressurization loading as these stresses will vary across the surface location. Stress distribution also occurs as loading tend to move from the more flexible portions of the base to the portions that are more rigid, an effect that is known as “stress redistribution”. [20].

In any vessel that is pressurized, whether from the outside or the inside volume, a number of stresses might be active within the wall. There are the three principal stresses:

$$\sigma_x = Longitudianal\ stress$$

$$\sigma_\varphi = Circumferential\ stress$$

$$\sigma_\varphi = Radial\ stress$$

The other two stresses that might be acting are the bending and shear stresses. The radial stress is the result of the pressure force acting over the entire surface and is a compressive stress. Normally in thin walled vessel this stress is small and it can be therefore ignored. Not considering this stress simplifies the combining stress method as it becomes biaxial. For thicker wall where R (m/t<10) the radial stress cannot be ignored and the governing equations are different from the one used to find membrane stresses. A good design rule is to allow a major safety factor so to compensate for unknown stresses. There are various stress theories the study when the combined stresses in a pressurized structure are bound to lead to failure. The main one we shall discuss are the maximum stress theory and the maximum shear stress theory. The maximum stress theory is the oldest and simplest to apply [20]. In this theory only maximum principal or normal stress is considered to assess if the material is bound to fail under load and it is used for membrane type of stresses biaxial in nature. While simpler to apply maximum stress theory require the use of a higher safety factor and the other disadvantage is that is good at predicting brittle material failure but is less effective in capturing the behaviour of ductile materials as these tend to fail by shearing at 45° to the applied force. The four

states of biaxial stresses, biaxial tension (quadrant I), tension (quadrant II), bi-axial compression (quadrant III), and compression (quadrant IV):

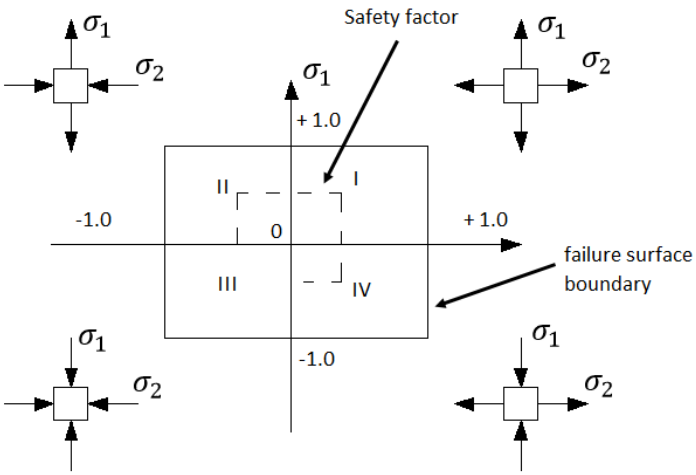


Figure 4: Bi-axial stresses states

Maximum shear stress theory

This theory is based on the assumption the material will yield in the planes subjected to maximum stress, more specifically the starting point will coincide with the maximum shear stress in that point reaches one-half of the uniaxial yield strength [20]. Therefore for a biaxial stress where σ_1>σ_2 the material will yield when the following condition is satisfied:

$$\frac{\sigma_1 - \sigma_2}{2} = \frac{F_y}{2}$$

ASME Code, section VIII, Division 2, use the maximum shear stress. It is used as it simple and is very close the experimental results. This theory can also be applied to tri-axial states of stress where material will fail as soon as the difference between maximum and minimum stress is equal to one-half of the yield stress. When $\sigma_1 > \sigma_2 > \sigma_3$the maximum shear stress will be$\frac{(\sigma_1 - \sigma_3)}{2}$. Material will start yielding:

$$\frac{\sigma_1 - \sigma_3}{2} = \frac{F_y}{2}$$

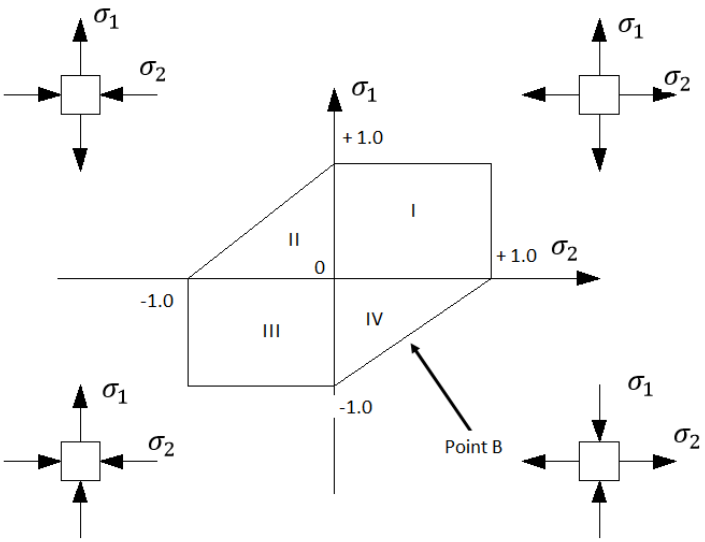


Figure 5: Plot of maximum shear stress theory

If we look at point B we can see how maximum shear stress theory in the above plot predicts material yielding at earlier points in quadrant II and IV. For point B $\sigma_2 = -\sigma_1$ so shear stress becomes: $\sigma_2 - (-\sigma_1)/2$ which is $\sigma_2 + \sigma_1/2$ that is half the stress which would cause yielding in maximum stress theory.

Comparing between the maximum stress and maximum shear stress theory.

For uniaxial stresses or for stresses where the principal stress is much bigger in magnitude compared to the others both theories are in agreement. The two theories come to a difference when both principal stresses are equal in magnitude. For istance in the maximum stress theory it is the largest stress, the circumferential stress, $\sigma_\emptyset$, that should determine the thickness of the pressurized cylinder.

For the maximum shear stress theory the controlling stress wo`uld be equal to ½ the difference between maximum and minimum stress:

If the maximum shear stress is $\sigma_\emptyset = \frac{PR}{t}$ and the minimum stress is the radial stress, $\sigma_r = -P$ it follows that the maximum shear stress = $\frac{\sigma_\emptyset - \sigma_r}{2}$.

In ASME Code, section VIII, Division 2 stress intensity indicates a stress which is equal twice the maximum shear stress. As shear stress is ½ the yield stress only then stress intensity exceeds the yield strength of the material.

In this example stress intensity = $\sigma_{\emptyset} - \sigma_r$ and $\sigma_{\emptyset} - \sigma_r = \frac{PR}{t} + P$.

Both theories lead to similar results and can be used provided the pressured vessel has a thin wall and therefore can be assumed to have a biaxial stress.

2.4 Categories and type of failures in pressured vessels.

There are several reasons why a vessel stressed by the fluid generated pressure fails. Each failure has modality and can fall into one of four major categories [20]:

1. **Material** – Wrong material for the application or the material has defects.
2. **Design** – Incorrect design and insufficient design testing.
3. **Manufacturing** – Insufficient building quality and quality control procedures. For example welding, heat treatment, assembly.
4. **Service** – User changes service conditions, untrained equipment use in the inappropriate conditions. Some type of service require special attention for istance:
   a. Design carries mortality risk
   b. Fatigue can occure during cycled use
   c. Brittle (low temperature) operation
   d. High temperature operation
   e. High shock and vibrations
   f. Vessel contect (corrossive, reactive etc.) for example: Hydrogen, Ammonia, Compressed air, Caustic, Chlorides.

Type of failures

1. **Elastic deformation** – Vessel buckling is prevented by elastic stability, vessel geometry, m suited material properties.

2. **Brittle fracture** – Can occure at low – intermediate temperatures conditions which might also accentuate even minor mateiral flaws.

3. **Excessive plastic deformation** – ASME Code, section VIII, Division 2 are intended to frame the design in a region of non plastic deformation in order to mininimise the occurrence of this type of failure.

4. **Stress rupture** – Fatigue or cycling loading can lead to creep deformation. Creep is a type-dependent phenomenon while fatigue a cycle dependent.

5. **High strain** – Particularly in lower strength/high ductile materials even low cycle fatigue can induce localised high strain that can eventually lead to failure.

6. **Stress corrosion** – Is well know that corrossive, aggressive materials can lead to corrosion cracking (chlorides in stainless steel, for example). In such application materials and conditions of use are very important in ensure long term reliability.

4. **Corrosion fatigue** – This can occure when corrosion is active on a fatigued structure and fatigue can deteriorate material reducing the material resistance. Surface can become pitted and cracks can propagate as a result of corrosion weaking the performance against fatigue which ultimatly lead to failure.

Safer design is the result of taking into account all these type of failures creating contingecies that allow safety factors to prevent the assembly ever entering a dangerous condition. Setting compatible stress magnitude compliancies is not enough, the overall lifetime conditions must not be allowed to compromise the integrity of the build.

Stresses in pressurised vessels are the results of loadings and forces applied by the pressurised fluids they contain (on top of the other possible loadings that might come from gravity, attached structures, weather conditions, high earthquake risk location, high termal excursions, etc.)

Loads can be general, in the way ther are applied over wide area of the strucure or localised, they both can produce membrane and bending stresses and must be added to esablish safe allowable stresses. The major component of stress direction can vary depending on conditions. For example a big vessel is exposed to the wind and the wind generates a tension along the longitudinal axis of the structure that has a tension nature on face that is facing the wind and compressive and opposite side (local membrane stresses and bending stresses). The design ought to understand all the loading generated and come with the worst probable stress combination that can be used as a reference to specify conditions so that bearable combined stress is higher by a safety factor S_f.

There is also another important distiction to make. Stresses that are applied continuosly and uniformly across the entire section of the vessel are *primary* stresses. The stresses generated by pressure, for example, are primary stresses and will cause failure if they exceed the material design criteria but the stresses from the inward radial load could be either primary if unrelenting or secondary if relenting. Also important to keep in mind that this distinction can be applied in ductile materials as for brittle material there is no difference between primary and secondary loads [20].

Loading must also be considered in the time domain as it might be steady (continuous), or non steady and therefore temporary. A stress induced by sismic activity will fade off once the sismic activity is finished therefore a temporary higher load might be acceptable if the geological statistical data of the area indicate that is a rare short lasting event, obviously by design vessel should not fail, this is the reason why a higher value of allowable stress might be chosen, typicall one third higher.

For general loads unformly applied across the entire section the allowable resulting stresses should be lower.

2.5 Loading generic classification

A Load Category

1. General loads (applied over entire structure practically continuosly)

   1a. Pressure loads (internal or external pressure)

   1b. Moment loads (Wind, sesmic activity, installation)

   1c. Compressive and tensile loads (dead weight from content, secondary structures fitted to the vessel, piping)

   1d. Thermal loads (for example a pipe heater installed on the outlet)

2. Local loads (reaction from supports, pipes, attached structures, attached equipment)

   2a. Radial loads (inward and outward)

   2b. Shear loads (longitudinal and circumferential)

   2c. Torsional loads

   2d. Tangential loads

   2e. Moment loads (longitudinal and circumferential)

   2f Thermal loads

B Type of loads

1. Steady loads (Long term; continuous)

   1a. Pressure (internal or external)

   1b. Dead weight

   1c. Vessel content

   1d. external loading (piping, equipment attached)

   1e. loading transferred from supports

   1f. Thermal loads

   1g. Wind loads

2. Non steady loads (short term; variable)

   2a. Postmanufacturing stress testing

   2b. Sismic activity

   2c. Installation (stresses generated for example from crane pulling)

   2d. Transportation

   2e. Thermal loads

2.6 STRESS

The pressure vessel thickness calculated by formula for pressure alone are no sufficient to account for all the loadings that a structure might be subjected to. Detailed calculation should characterize each single loading separately and it must then combine them to assess the total stress that the part will see in the designed lifetime.

Stresses that act on a pressure vessel can be separated into classes [20] according the tpye of load that generates them and their hazards. Not only the Single stresses but also the combine total stress must be managed at certain level identified in the design. Relenting loads that have a self-containing nature will produce secondary stresses while unrelenting load will generate primary stresses. General loadings will generate primary membrane and bending stresses while local loads will produce local membrane and bending stresses. Primary stresses must be kept at a lower magnitude compared to secondary stresses.

Type of Stress

There are enough type of stresses to sometime confuse even a designer that deal regularly with pressurized vessels. Stresses are organised in three major classes and further distinguished depending on the effect on the structure.

1. Tensile
2. Compressive
3. Shear
4. Bending
5. Bearing
6. Axial
7. Discontinuity
8. Membrane
9. Principal
10. Thermal
11. Tangential
12. Load induced
13. Strain induced

14. Circumferential
15. Longititudinal
16. Radial
17. Normal

Classes of Stresses

1. Primary stress
    a. General:
        - Primary general bending stress Pm
        - Primary general bending stress Pb
    b. Primary local stress, PL

2. Secondary stress
    a. Secondary membrane stress, Qm
    b. Secondary bending stress, Qb

3. Peak Stress, F

Primary general stress

These stresses act on the entire vessel cross section as a result of internal or external pressure and they are very dangerous to the structure integrity. Primary stresses can be calculated separately as membrane and bending stresses. These distiction is made so that design can allow the primary bending stress might be allowed to wonder highly than the primary membrane stress [20]. If primary stresses are allow to grow excessively than the material can either fail or be subjected to excessive deformation.

Primary general membrane stresses, Pm.

These stressed occur far away from discontinuities like head-shell interesections, cone-cylinder interesections, nozzles and supports as for example:

a. Circumferential and longitudinal stress pressure dependent
b. Compressive and tensile axial stresses result from the wind action
c. Longitudinal stress due to the centrale bending of long vessel over the supporting saddles
d. Membrane stress in the centre of the flat head
e. Nozzle wall membrane stress
f. Axial compression stress as a result of the structural weight

Primary general bending stress, Pb.

These stresses are the result of sustained loads and can result in the vessel collapse. Some vessel areas are more prone to develop such stresses like for example:

a. Bending stress in the centre of the flat head of dished head
b. Bending stress in the shallow conical head
c. Bending stress in the closely spaced opening ligaments

Local primary membrane stress, P_L

This is the combination of two stresses: primary membrane stress, Pm plus secondary membrane stress, Qm resulting from stustained loads and are grouped together to ensure they are kept low during the design.

Local primary stresses have self-limiting nature as when the material reaches yield strength the load spreads on contiguous stiffer areas but as any deformation that might result from the material yielding the allowable magnitude by design has to be lower.

Secondary stress

The important characteristic of secondary stress is its nature truly self-limiting and in general do not lead to structural failure also because they tend to occur at the junctions of major vessel components. Secondary stresses can originate from vessel attachment on the shell of the vessel, for example a long and heavy nozzle not properly supported can produce stresses at the junction with the wall and can be strain-induced. Discontinuity stresses can also be considered as secondary stresses as long they do not extend to far ($2.5\sqrt{R_m T}$) and also cannot be closed to discontinuites by the same distance.

Secondary membrane stress, Qm

a. Juncture flange axial stress
b. Thermal stresses
c. Head knucle area membrane stress
d. Local loads membrane stress

Secondary membrane stress, Qb

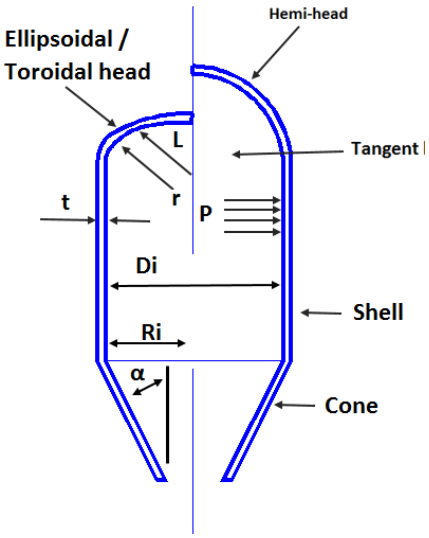
a. Bending stress at major structural discontinuity: for example nozzles and lugs

b. Nonuniform stress distribution in a thick-walled vessel as a result of interna pressure

c. Thick-walled nonuniform stress distribution as are result of internal pressure

d. Discontinuity stresses at stiffening or support rings

General design vessel formulas:



P = Internal pressure, psi

Di, Do = inside/outside diameter, in.

S = Calculated stress

E = joint efficiency

L = crown radius

Ri, Ro = inside/outside radius, in

K, M = coefficients

σ_x = Longitudinal stress, psi

σ_θ = Circumferential stress, psi

Rm = mean radius of shell, in

t = thickness of shell

r = knucle radius, in

1. For pressure < 3,000 psi
2. Cylindrical shells where $t \leq 0.5R_i$ or $P \leq 0.385SE$
3. Sphericals shells and hemispherical heads $t \leq 0.356R_i$ or $P \leq 0.385SE$

Formulas [20]

Part	Stress Formula	Thickness, t		Pressure, P		Stress, S	
		I.D.	O.D.	I.D.	O.D.	I.D.	O.D.
Shell							
Longitudinal [1, Section UG-27(c)(2)]	$\sigma_x = \frac{PR_m}{0.2t}$	$\frac{PR_i}{2SE + 0.4P}$	$\frac{PR_o}{2SE + 1.4P}$	$\frac{2SEt}{R_i - 0.4t}$	$\frac{2SEt}{R_o - 1.4t}$	$\frac{P(R_i - 0.4t)}{2Et}$	$\frac{P(R_o - 1.4t)}{2Et}$
Circumferential [1, Section UG-27(c)(1); Section 1-1(a)(1)]	$\sigma_\phi = \frac{PR_m}{t}$	$\frac{PR_i}{SE - 0.6P}$	$\frac{PR_o}{SE + 0.4P}$	$\frac{SEt}{R_i + 0.6t}$	$\frac{SEt}{R_o - 0.4t}$	$\frac{P(R_i + 0.6t)}{Et}$	$\frac{P(R_o - 0.4t)}{Et}$
Heads							
Hemi sphere [1, Section 1-1(a)(2); Section UG-27(d)]	$\sigma_x = \sigma_\phi = \frac{PR_m}{2t}$	$\frac{PR_i}{2SE - 0.2P}$	$\frac{PR_o}{2SE + 0.8P}$	$\frac{2SEt}{R_i + 0.2t}$	$\frac{2SEt}{R_o - 0.8t}$	$\frac{P(R_i + 0.2t)}{2Et}$	$\frac{P(R_o - 0.8t)}{2Et}$
Ellipsoidal [1, Section 1-4(c)]	See Procedure 2-4	$\frac{PD_iK}{2SE - 0.2P}$	$\frac{PD_oK}{2SE + 2P(K - 0.1)}$	$\frac{2SEt}{KD_i + 0.2t}$	$\frac{2SEt}{KD_o - 2t(K - 0.1)}$	See Procedure 2-2	
2:1 S.E. [1, Section UG-32(d)]	"	$\frac{PD_i}{2SE - 0.2P}$	$\frac{PD_o}{2SE + 1.8P}$	$\frac{2SEt}{D_i + 0.2t}$	$\frac{2SEt}{D_o - 1.8t}$	"	
100%–6% Torispherical [1, Section UG-32(e)]	"	$\frac{0.885PL_i}{SE - 0.1P}$	$\frac{0.885PL_o}{SE + 0.8P}$	$\frac{SEt}{0.885L_i + 0.1t}$	$\frac{SEt}{0.885L_o - 0.8t}$	"	
Torispherical L/r < 16.66 [1, Section 1-4(d)]	"	$\frac{PL_iM}{2SE - 0.2P}$	$\frac{PL_oM}{2SE + P(M - 0.2)}$	$\frac{2SEt}{L_iM + 0.2t}$	$\frac{2SEt}{L_oM - t(M - 0.2)}$	"	
Cone							
Longitudinal	$\sigma_x = \frac{PR_m}{2t\cos\alpha}$	$\frac{PD_i}{4\cos\alpha\,(SE + 0.4P)}$	$\frac{PD_o}{4\cos\alpha\,(SE + 1.4P)}$	$\frac{4SEt\cos\alpha}{D_i - 0.8t\cos\alpha}$	$\frac{4SEt\cos\alpha}{D_o - 2.8t\cos\alpha}$	$\frac{P(D_i - 0.8t\cos\alpha)}{4Et\cos\alpha}$	$\frac{P(D_o - 2.8t\cos\alpha)}{4Et\cos\alpha}$
Circumferential [1, Section 1-4(e); Section UG-32(g)]	$\sigma_\phi = \frac{PR_m}{t\cos\alpha}$	$\frac{PD_i}{2\cos\alpha\,(SE - 0.6P)}$	$\frac{PD_o}{2\cos\alpha\,(SE + 0.4P)}$	$\frac{2SEt\cos\alpha}{D_i + 1.2t\cos\alpha}$	$\frac{2SEt\cos\alpha}{D_o - 0.8t\cos\alpha}$	$\frac{P(D_i + 1.2t\cos\alpha)}{2Et\cos\alpha}$	$\frac{P(D_o - 0.8t\cos\alpha)}{2Et\cos\alpha}$

2.7 Maximum allowable pressure:

Notation:

S_a = Allowable stress (ambient temperature), psi

S_{DT} = Allowable stress (design temperature), psi

S_{CA} = Clad material allowable stress (ambient temperature), psi

S_{CD} = Clad material allowable stress (design temperature), psi

S_{BA} = Base material allowable stress (ambient temperature), psi

S_{BD} = Base material allowable stress (design temperature), psi

C_a = Corrosion allowance, in.

T_{sc} = Thickness of shell corroded, in.

T_{sn} = Thickness of new shell, in.

T_{hc} = Thickness of head corroded, in.

T_{hn} = Thickness of head new, in.

T_b = Thickness of clad material base portion, in.

T_c = Thickness of clad material, in.

R_n = Inside radius, new, in.

R_c = Inside radius, corroded, in.

R_o = Outside radius, in.

D_n = Inside diameter, new, inch.

D_c = Inside diameter, corroded, in.

D_o = Outside diameter, in.

P_M = MAP, maximum allowable pressure, psi

P = Pressure (design), psi

P_s = Shop hydro pressure, psi

P_F = Field hydro pressure, hot and cold, psi

E = Joint efficiency

Maximum allowable working pressure (MAWP):

The MAWP defines the maximum pressure that the vessel is allowed to operate in working conditions and at the design temperature and in the hot and corroded conditions. This pressure value should be part of the vessel information carried by the front nameplate. This pressure value is the smallest value calculated over the entire structure and is adjusted by a factor that takes into account the static head calculated from that part and the top of the vessel. Every single element of the vessel is evaluated at the nominal thickness exclusive of the corrosion allowance. It is possible to

design for different temperatures if required by the final use. It is important that the pressure relieve valve magnitude is identified taking into account design and final usage conditions. Therefore we shall define:

Maximum Allowable Pressure (MAP):

This the maximum pressure that can be applied to the weakest part in cold conditions and without taking into account corrosion and other loading conditions.

Design pressure:

It is the maximum pressure for the vessel component that sees the worst combinations of pressure and temperature conditions that the structure will be subjected during normal operating conditions [20]. Maximum pressure difference inside to outside and in between chambers sharing a wall should be considered. Thickness required from the loading effect of static head and other loadings is additional to the design pressure.

Design temperature:

For most designs this is the temperature at which the design pressure has been calculated, but, as temperature is variable there will be a maximum temperature and minium design operating temperature for every vessel. The MDMT will be the minimum vessel design temperature and is calculated for every single part. External pressure charts will identify the maximum pressure that can be exerted externally on the vessel.

Operating pressure:

This is normally the pressure at the top of the vessel and it should be lower than the maximum allowable working pressure, design pressure, or the set level of any pressure relief acting device.

MAWP, correded at design temperature Pw, equations:

Shell:

$$P_w = \frac{S_{DT} E t_{sc}}{R_c + 0.6 t_{sc}}$$

$$P_w = \frac{2 S_{DT} E t_{hc}}{D_c + 0.2 t_{hc}}$$

MAP, new and cold, Pm.

Shell:

$$P_M = \frac{S_a E t_{sn}}{R_n + 0.6 t_{sn}}$$

2:1 S.E. Head:

$$P_M = \frac{2 S_a E t_{hn}}{D_n + 0.2 t_{hn}}$$

Shop test pressure, Ps:

$$1.3\ P_W \left[\frac{S_a}{S_{DT}}\right]$$

Field test pressure, P_F

$$P_F = 1.3P$$

Stresses in heads as a results from internal pressure loading:

Notation:

L = Crown radius, in.

r = Depth of head, in.

R_L = Latitudinal radius, in.

R_m = Meridional radius curvature, in.

σ_θ = Latitudinal stress, psi

σ_x = Latitudinal stress, psi

P = Internal pressure, psi

Equations:

Ellipsoidal heads R_L and R_m lengths:

Equatorial:

$R_m = \frac{h^2}{R}$ = Internal pressure, psi

$R_L = R$

At any X point:

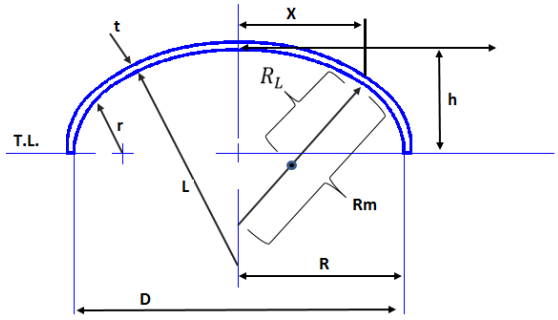
$R_L = \sqrt{\frac{R^4}{h^2}X^2(1 - \frac{R^2}{h^2})}$

$R_m = \frac{R_L^3 h^2}{R^4}$

Notes:

1. Heads can fail when R/h ratio exceeds 1.42 and the kuckle hoop latitudinal stress becomes compressive.
2. There are three categories classifying head types: hemispherical, torispherical and ellipsoidal. Hemispherical heads are calculated as spheres. Torispherical and ellipsoidal heads are calculated with the following equations[20]:

Fig. 6



TORISPHERICAL HEADS			
σ_x		σ	
At Junction of Crown and Knuckle			
$\sigma_x = \frac{PL}{2t}$		$\sigma_\phi = \frac{PL}{4t}\left(3 - \frac{L}{R}\right)$	
In Crown			
$\sigma_x = \frac{PL}{2t}$		$\sigma_\phi = \sigma_x$	
In Knuckle			
$\sigma_x = \frac{PL}{2t}$		$\sigma_\phi = \frac{PL}{t}\left(1 - \frac{L}{2r}\right)$	
At Tangent Line			
$\sigma_x = \frac{PR}{2t}$		$\sigma_\phi = \frac{PR}{t}$	

ELLIPSOIDAL HEADS			
σ_x		σ	
At Any Point X			
$\sigma_x = \frac{PR_L}{2t}$		$\sigma_\phi = \frac{PR_L}{t}\left(1 - \frac{R_L}{2R_m}\right)$	
At Center of Head			
$\sigma_x = \frac{PR^2}{2th}$		$\sigma_\phi = \sigma_x$	
At Tangent Line			
$\sigma_x = \frac{PR}{2t}$		$\sigma_\phi = \frac{PR}{t}\left(1 - \frac{R^2}{2h^2}\right)$	

2.7.1 Optimum vessel proportions:

In general vessel design one of the common questions to answer is what is the optimal proportions expressed in L/D ratio will allow for minimum weight for the desired vessel volume. Obviously the geometrical shape that maximises volume versus surface area and weight is the sphere, but unfortunately building perfect spheres is quite difficult therefore this shape is not often choosen unless the volume is quite high or there is a specific reason that overrides the cost-time considerations. The L/D ratio is not just a geometrical factor but it also depends of other factors like pressure magnitude, allowable stress, corrossion allowance, joint efficiency. In the literature, Brownell and Young suggest that up to 2 inch wall thickness vessel a good ratio L/D is 6, if more than 2 inch than L/D factor increases to 8. Other approches consider breakdown of pressure versus L/D ratio. For example, L/D ratio 3 up to 250 pressure (PSIG), 4 if pressure ranges from 250 to 500 and 6 if more than 500. This an improvement that can be furtherly perfected. Storage volume is also important, so for example, for high hold up volumes it is better to design horizontal vessels while for small requirements upright vessels are generally better [20].

Economical L/D ratio range typically between 1 and 10 beyond it is not recommended as it is impractical for most applications.

A method example follows, bearing in mind that the exact economics are much harder to calculate as there are other variables affecting cost:

First the necessary variables are defined, these are: Volume (V), Pressure (P), Corrosion allowance (C), Allowable stress (S), Joint efficiency (E). First F_1 is calculated then L/D ratio is calculated from specific tables then from D and V the required length can be computed.

Optimum vessel proportions for Vessel 2:1 S.E. Heads

Notation

V = Volume of Vessel, cu ft

P = Lnternal pressure, PSIG

L = Length, T-T, ft

T = Shell thickness, in

W = Vessel weight, lb

D = Diameter, ft

C = Corrosion allowance, in.

A = Surface area, sq ft

F_n= Vessel ratios

S = Allowable stress, psi

E = Joint efficiency

w = Unit weight of plate, PSF

L_e= Equivalent length of cylinder equal to vessel volume with (2) 2:1 S.E. heads

h = Height of the cone, ft

R = Radius, ft

C_1, K_1 = Constant for elipsoidal heads

Equations:

L_e= L + 0.332D

$$V = \frac{\pi D^3}{12} + \frac{\pi D^2 L}{4}$$

$$D = \sqrt[3]{\frac{4V}{\pi(0.333 + \frac{L}{D})}}$$

$$W = A_w$$

$$A = 2.18D^2 + \pi DL$$

$$t = \frac{PR}{SE - 0.6P} + C$$

$$L = \frac{4V}{\pi D^2} - \frac{D}{3}$$

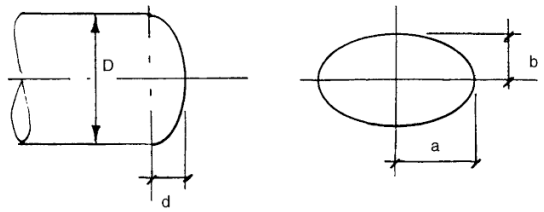
$$F_1 = \frac{P}{CSE}$$

$$F_2 = C(\frac{SE}{P} - 0.6)$$

Diameter for different L/D Ratios:

L/D	D
3	$\sqrt[3]{\frac{6V}{5\pi}}$
1	$\sqrt[3]{\frac{12}{13\pi}}$
5	$\sqrt[3]{\frac{3V}{4\pi}}$
6	$\sqrt[3]{\frac{12V}{19\pi}}$
7	$\sqrt[3]{\frac{6V}{11\pi}}$
8	$\sqrt[3]{\frac{12V}{25\pi}}$

Atmosferic tank proportions:



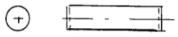
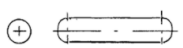
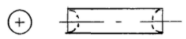
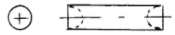
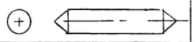
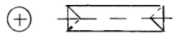
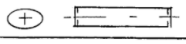
$$K_1 = \frac{2d}{R}$$

$$K_2 = \frac{b}{a}$$

$$C_1 = 2 + \frac{K_1^2}{\sqrt{1-K_1^2}} \ln\left(\frac{1+\sqrt{1-K_1^2}}{1-\sqrt{1-K_1^2}}\right)$$

Note: For 2:1 S.E. Heads, $C_1 = 2.76$ and $K_1 = 0.5$.

Optimum tank proportions [20]:

Case	Optimum Proportions	Volume
Cylinder with flat ends 	$L = D$	$2\pi R^3$
Cylinder with ellipsoidal heads 	$L = R(C_1 + 4K_1)$	$\pi R^3\left(\frac{3C_1 - 8K_1}{3}\right)$
Cylinder with internal ellipsoidal heads 	$L = R(C_1 + 4K_1)$	$\pi R^3\left(\frac{3C_1 + 8K_1}{3}\right)$
Cylinder with internal hemi-heads 	$L = 8R$	$6.66\pi R^3$
Cylinder with conical ends 	$h = 0.9R$ $L = 0.9R$	$1.5\pi R^3$
Cylinder with internal conical ends 	$h = 0.9R$ $L = 3.28R$	$2.68\pi R^3$
Elliptical tank with flat ends 	$L = 2K_2 a\sqrt{\frac{2}{1+K_2^2}}$	$2K_2^2\pi a^3\sqrt{\frac{2}{1+K_2^2}}$

2.8 Bottle Testing procedures

2.8.1 Visual Inspection

Visual inspection describes here a range of optical test performed on the final bottle to record conditions and microscopic feature locations particularly useful when comparing a burst bottle versus a standard specimen. The sample is prepared by cutting sections and region using various means, like band saw trying to minimise damage artefacts in the cut surface. Within the bulk of the material operator will look for imperfections like intra-structural voids, inclusions, signs of contamination discontinuities and general imperfections.

2.8.2 Thickness measurements

The material performance of the bottle base is affected by how much the material moves in the mould during blowing and by the final thickness that is achieve in the different complex region of the base. These measurement can be achieved by various means, but a typical instrument is the MagnaMike 8600 which uses a hall sensor to detect the distance from sensor to a metal ball. Two types were employed, 1.58 mm size 80TB1 and the 3.17 mm 80TB2, and these two sizes can cover thickness from up to 2.03 and 6.1 mm maximum sample thickness. The metal ball is simply dropped in the bottle base via the neck of the bottle and then the base is brought close to the sensor. The sensor magnetically attracts the ball to the base and measure the distance sensor to ball which equates to the thickness of the material. It is important that the ball is right on the longitudinal axis of the sensor to maximise accuracy. Where the valley is very convoluted this sometime can be difficult, nevertheless the measurement is still quite reliable.

A topographic map with critical points can be defined at different bottle based and can be later used to evaluate cracks and failures in combination with other test results.

2.8.3 Environment stress cracking techniques (ESC)

ESC affects PET bottles that contain carbonated drink and have a history of exposure to alkaline solutions, detergents, sanitizers while being stored under pressure during their shelf life. ESC can be managed by increasing bottle robustness and by managing the bottles in a way that reduces the chance of coming in contact with materials that favour ESC [6]**.**

In this test the PET bottle is exposed to the aggressive action of corrosive fluids that accelerate crazing process at much lower stress field. The caustic bath has a concentration of 0.2% caustic soda solution and the bottle is pressurized at 5.3 Bar and bottle failure is monitored over ten minutes. Within all plastic failures 15% is estimated to originate from environmental stress cracking. [9]

2.8.4 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry allows us to characterize the degree of crystallinity the melting and softening behaviour of the polymer, this is a very important test when characterizing the material mechanical properties and burst performance of the bottle. The level of crystallinity can be traced to what happened in the mould therefore alighting issues of process inconsistencies. Also if reground material addition is suspected DSC can provide information to help identifying re-work addition. [9] DSC is an important thermal analysis technique. As small quantities of the sample (mg) is heated in the instrument the specimen temperature rises by an amount that is function of the specific heat of the sample (for a given energy input). The energy absorption evolution of the sample during the test therefore can produce important information that characterizes the identity of the material showing melting and softening behaviour of semi-crystalline thermoplastic materials, transition temperatures like glass transition temperatures, re-crystallisation temperature, crystalline melting point or degradation temperature.

Other information that can be extracted relates to the sample material thermal and process history

of the material and even contamination. In fact DSC is very sensitive to contamination and since eliminating contamination from material grinding is difficult and maintaining material homogeneity is very important to ensure consistent mechanical process performance DSC was a key test for our work.

DSC methodology:

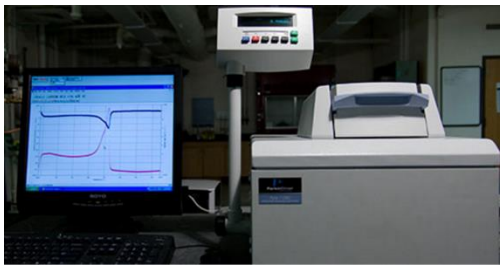


Figure 7: DSC equipment

This DTC holds the sample in a heated chamber and precisely monitors the energy absorbed by the sample as it gradually warms at the defined heating rate. If (Cp) is the heat capacity, dH/dt is the scanning rate, T the temperature, t the time, then (Cp) is measured directly from (Cp = dH/dT) as is function to the rate of heat absorption dH/dt according the

following equation:

$$dH/dt = dH/dT \times dT/dt$$

During the heating ramping up eventually the sample reaches the melting temperature, during this phase transition stage in the plot which relates temperature to heat capacity an endothermic peak appears, since Cp is specified per unit weight and the samples mass is known therefore DSC is quantitative and area of this peak is equal to heat of reaction ∇Hf in joules /gram. Similarly during cooling the exothermic reaction shown in the plot will represent the recrystallization reaction. Finally in the curve the step will represent the glass transition of the sample.

Before running the specimen is to be calibrated for temperature and ∇Hf using materials of known certified properties.

A small sample (ca. 10 mg from bottle, preform, pellet) is cut directly and weighed before being placed in the instrument. The sample is from +40°C to +400°C with a heating rate of 20.00 °C per minute. The sample holding cavity is filled with inert nitrogen. The PC records will record the necessary data to calculate heat of reaction and melting peak values.

DSC can be used to characterize the thermal fingerprint property of the semi-crystalline material to identify the relative degree of crystallinity as this affects the mechanical performance.

2.8.5 Gel Permeation Chromatography (GPC)

As we are interested in characterising the mechanical performance of the assembly and molecular weight distribution of the PET polymer is important in making PET processable and affects the final mechanical property, GPC is another technique to be used to characterize the bottle material molecular mass and molecular mass distribution.

In GPC a small amount of the material is passed down a column which is filled up with a porous material. The polymer molecule of interact differently according to their relative size. The bigger particles have minor interaction and therefore leave the column earlier. The smaller particles are subjected to more intense interactions and therefore are slowed down and leaving the column later. The PC records the quantity proportional signal in the time domain and by calibrating the system against materials of known molecular weight it calculates the sample molecular weight from the time it took to travel the length of the column, as symbolically explained in the following schematic picture:

Red smaller molecular weight molecules exude later as they are slowed down by the porous material while the bigger green particles exude earlier producing the green shifted signal.

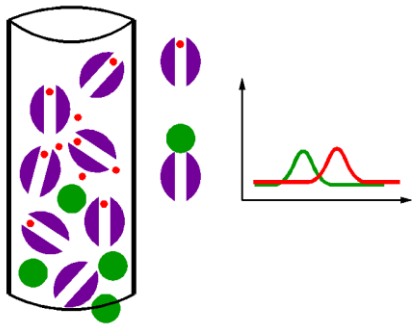


Figure 8: Smaller red molecule exude later as they are slowdown by the porous material

The chromatogram can be to calculate molecular weight, molecular weight distribution and the polydispersity index (PDI). PDI always has a value exceeding 1 but the more the polymer chains are uniform in the sample the closer to 1 the PDI value will be.

Sample Preparation

The solution is prepared by adding 10 mL of eluent to 20 mg of the sample and is left overnight to dissolve. Before testing the sample in the chromatographer the solutions are mixed and filtered using 0.45 µm PTFE membrane.

A calibration solution is used to prepare the instrument.

The molecular weights are expressed in 'PMMA equivalent' molecular weights.

2.8.6 Intrinsic viscosity (IV)

IV is a very monitoring important parameter, depends on molecular weight which affects the solution viscosity. This method needs high chemical consumption to be performed. Pet material to be analysed is dissolved in 3:2 phenol : 1,2 dichlorobenzene at a concentration of 0.5% and a temperature of 25°C. Once dissolved it is allowed to flow the flow time is measured against the solvent. The higher the PET molecular weight the higher the flow time the higher the IV value the slower rate of crystallisation.

Typically bottles IV value ranges between 0.65 to 0.85 dL/g. LIGHTER grade with different level of intrinsic viscosity are:

- Low viscosity (IV 0.76) for flater mineral water bottling.
- Medium viscosity (IV 0.8) carbonated drink
- High viscosity (IV 0.84) used for carbonated soft drink

Bottles for this application have an IV value of 0.8.

2.8.7 Mechanical test properties tests

2.8.7.1 Tensile strength

Tensile strength is the most common and the dumbbell shaped specimen is tested as described in ASTM D 638 procedure. This test will provide information regarding proportional limit, yield point (yield strength and elongation at yield), tensile strength at break point, elongation at break, elastic modulus (stiffness).

2.8.8 Fatigue test

As the bottle is thought will be pressurized a few tens of time we built a rig test equipment which would cycle the pressure in the bottle with a specific ramping program to test if a bottle that had passed the pressure test would fail under fatigue. A bottle from a pressure passed batched (no burst at 2.0 bar) was visually inspected and then connected to the automatic rig.

The test was carried out at 20°C temperature and the rig could be programmed to ramp up the pressure up to 2.5 bar in ca. five seconds, leave the bottle pressurized for a ten seconds and then vent the pressure fast with a low pressure drop pneumatic venting circuit. The maximum number of cycles was three hundred. The bottle was then visual inspected.

2.8.9 Literature review conclusion

Literature review has identified numerous studies investigating PET base bottle performance under pressure induced stress. These studies have examined many relevant characteristics including PET mechanical properties, best manufacturing practices, design and quality testing. It is not surprising that extensive research has been carried out as the carbonated drink industry heavily relies on PET

bottles to safely deliver its products to customers. However, while current bottle designs address pressure performance with some relative environmental induced pressure changes, less is known about PET bottle base performance under full repetitive pressure cycling (0 to 2 bar), conditions specified in our application. Therefore, the objective of the work reported here is to evaluate performance within these more challenging boundaries.

Chapter 3

Testing Results

Pet resin, preforms and blown bottle bases were tested using differential scanning calorimetry (DSC) and Gel Permeation Chromatography (GPC). In the DSC testing, samples from the different specimens were cut out and placed in the instrument. The DSC instrument measures the amount of heat required to increase the temperature of the sample over a specified range. The waveform of the recorded plot conveys important sample information, for example, melting and softening behaviour, transition temperatures and crystalline melting point. In GPC a small amount of the sample is passed down a column filled with porous material that interacts with the different sample particle size. Particles of a bigger size interact less with the porous material and are passed through the column earlier. Calibration against a known material allows us to characterize sample molecular mass and molecular mass distribution.

To clarify results a specimen thermal imprint profile is reported in Figure 9. Features have been highlighted for clarity in the example.

3.1 Differential Scanning Calorimetry (DSC)

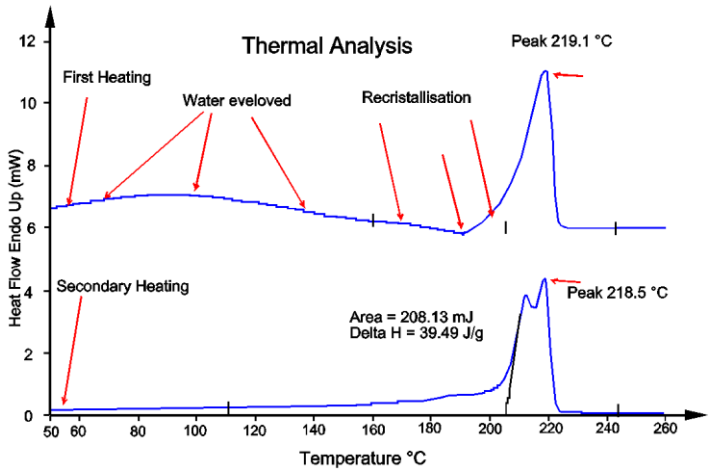


Figure 9: DSC thermal analysis graph example

DTC results from samples taken from the preform and bottle

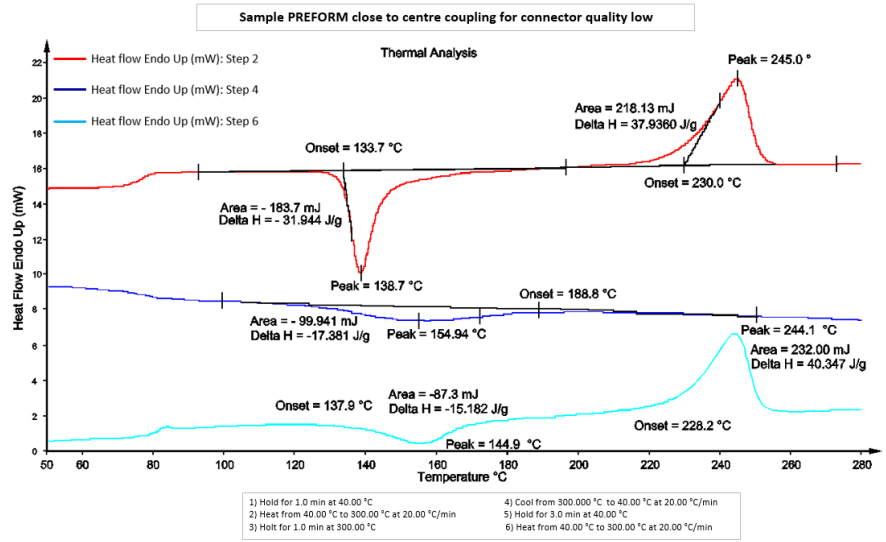


Figure 10: Preform sample close to connector lower quality

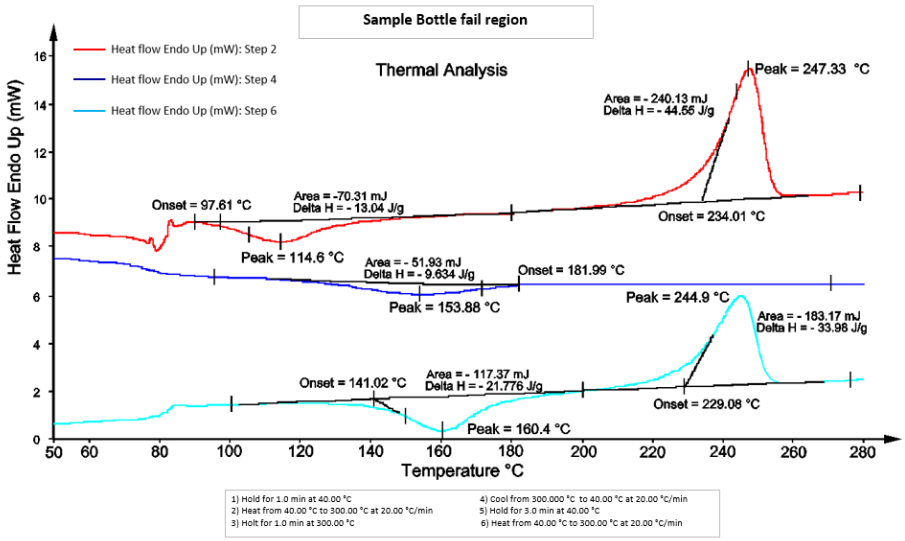


Figure 11: Bottle base fail region

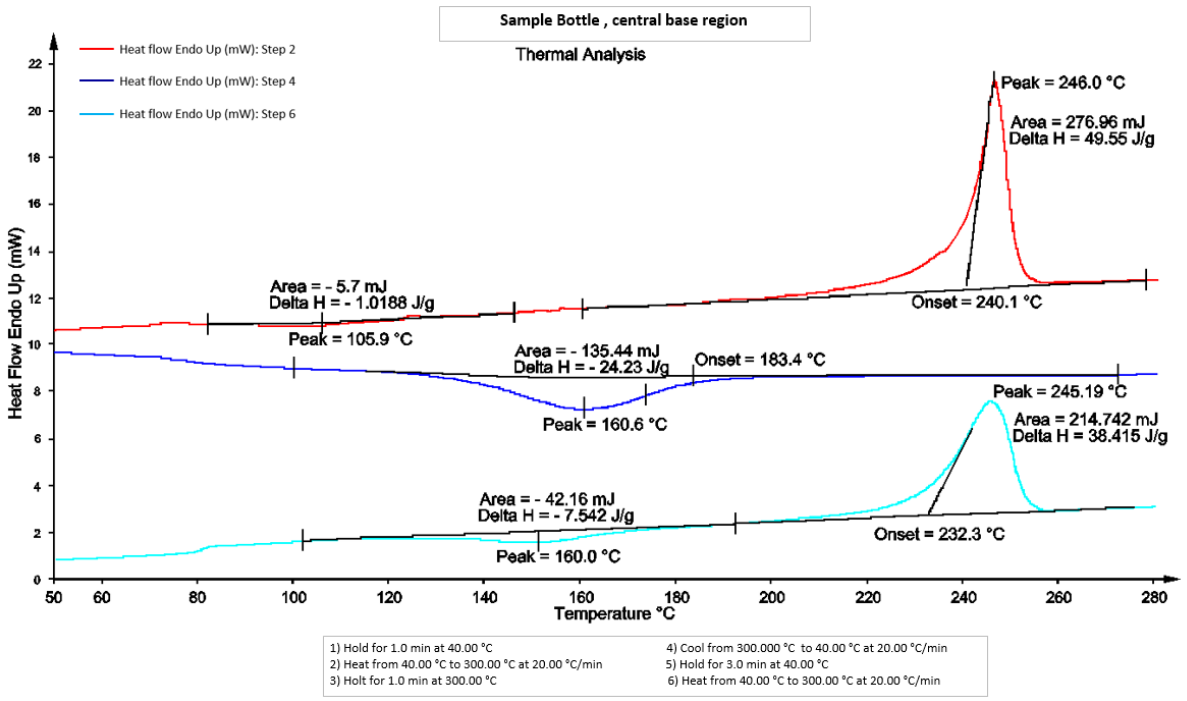


Figure 12: Bottle central base region

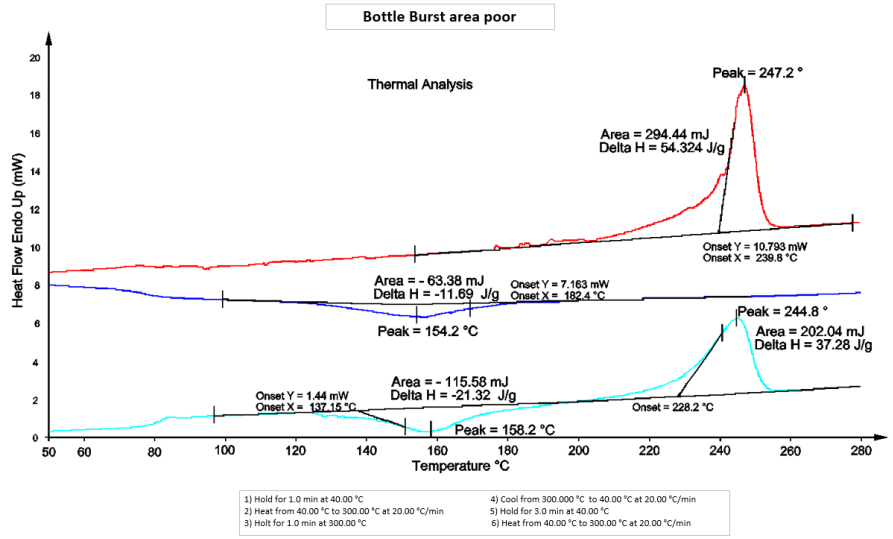


Figure 13: Burst / Outer Wall fail region

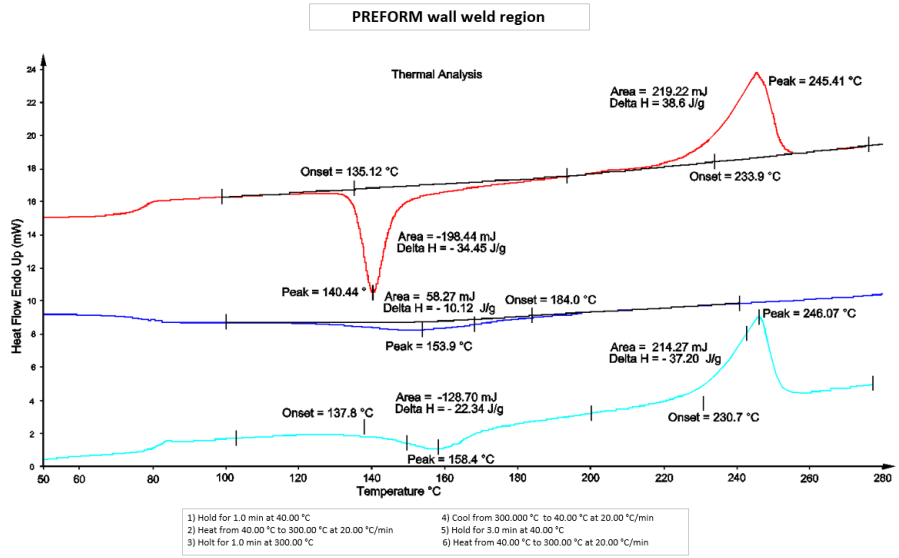


Figure 14: PREFORM wall weld region

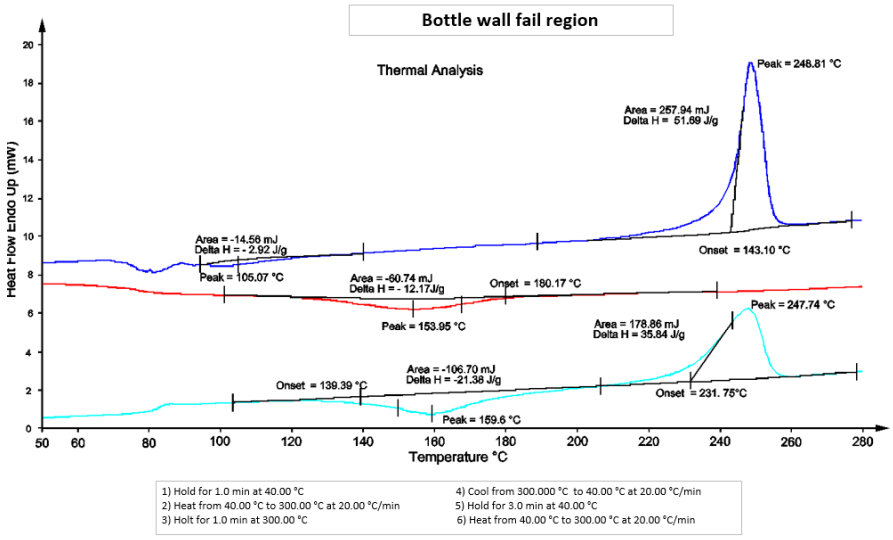


Figure 15: Bottle wall fail region

The above thermograms show a transition region between 82°C and 84°C which is the glass transition temperature for the PET material (Tg).

As the material melting point (Tm) ranges ca. 244°C to 248°C there is indication of PET has undergone some alteration of the original grade.

Note – In the DSC result plots attached the top trace (Step 2) is more representative of the material thermal history as it is received and is therefore a good indicator of processing characteristics. The lower trace (Step 6) obtained from the re-heat is more an indicator of the material itself.

The quantity of heat that is required to melt the material it is directly proportional to the specimen crystallinity level. The level of crystallinity derived from the re-heat is regarded as the natural level for the material. If we now divide the heat of fusion from the top (as-received) trace by the heat of fusion from the bottom (re-heat) trace we can calculate the relative crystallinity in the material which can be regarded as percentage of the the ideal value.

While there are number of processing parameters affect the sample crystallinity level, cooling rate is the predominat factor that plays a dominant role.

When the preform is formed in the injection moulding process, in general, the hotter the tool the greater the energy that is available to generate crystallisation therefore the greater the crystallinity level. When the crystallinity is higher the crystal lamellae are thicker and therefore require more heat to melt them. This means the heat of fusion is higher, as during the re-heat phase the crystallinity measure represents the natural level, if we divide moulded preform heat of fusion by the heat of fusion obtained during re-heat we can calculate the percentage of ideal crystallisation. Generally a level from 90 to 100 % is considered good, levels between 80 and 90% should be looked at as they can be improved and levels below 80% are likely to generate problems. To be noted that having level exceeding 100% is possible, even 110% but these levels are equally not desireble as they indicate a risk of brittlness which is detramental in this application. It is generally better to try and achieve crystallinity levels which are in line with the material natural levels.

The sample bases tested showed variable and high levels of relative crystallinity.

If material fails to achieve natural crystallinity level during moulding it will try and achieve during the test, this shows with a higher heat flow (mW) exothermic peak which in the plot the top trace is marked with the right smaller red circle (Recrystallisation) before the main endothermic melting peak.

No significant differences were observed between the poor batch and the current batch.

Now we have expected the that areas sampled close to the power connector where fractures occurred would exhibit to be quite amorphous and therefore producing a relatively high recrystallisation peak. This happened for the burst empty bottle Sample 2, however, the bottle burst Sample 19 exhibited less re-crystallisation indicating that it was more crystalline than Sample 2.

When the current batch was tested the filled bottle Sample 11 was in line with what expected but the empty bottle Sample 14 showed a similar recrystallisation response to the bottle Sample 19 that failed.

This variability indicates that the thermal process control stability can be better controlled. It is to be noted as the project is not currently fully operational the injection and blowing processes are subjected to continuos change-over between supplier formats and therefore re-setting optimal conditions is more difficullt, once the plants enter full production and minimise change over a better chance of controlling thermal and other process parameters should be easier.

3.2 Gel Permeation Chromatography (GPC)

During the testing sample appeared to produce clear solutions and did not have any problems neither with filtration nor with the cromaptograghy of any solutions.

In the first figure the plot of all refractive poor batch index chromatograms overlayed against Sample resin.

In the second figure the plot of all refractive current standard batch index chromatograms overlayed against resin. Plots are normalised respect to the area, the y-axis being a function of the weight fraction.

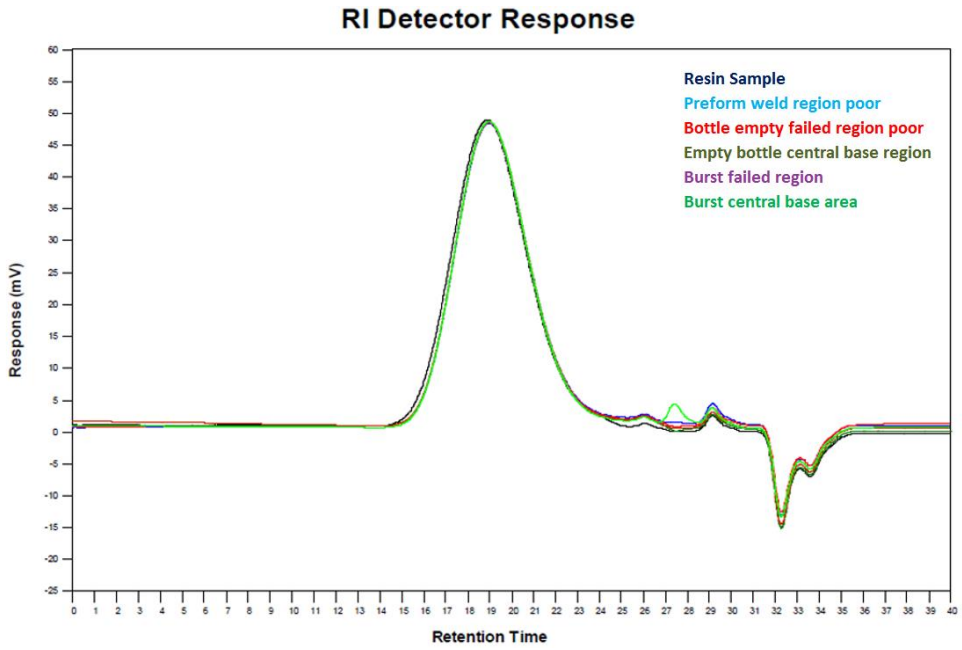


Figure 16: GPC plots of bottles and preforms

Results shown in Tables are summarised (calculated molecular weight averages and polydispersity Mw/Mn).

Poor Batch

Sample	Run No	Mw	Mn	Polydispersity
PET resin	07	41,600	15,700	2.7
repeat	20	41,600	15,700	2.6
Preform				
Weld region - poor	8	38,400	14,700	2.6
repeat	17	38,300	14,700	2.6
Bottle Empty				
Fail Region – Poor	9	38,600	14,800	2.6
repeat	22	38,600	14,900	2.6
Sample 2 Empty/				
Bottle base region emptu	10	38,300	14,700	2.6
repeat	15	38,400	14,800	2.6
Bottle burst				
Fail Region – Poor	14	38,500	14,800	2.6
repat	24	38,400	14,700	2.6
Bottle burst 2				
Base central region	12	38,600	14,800	2.6
repeat	25	38,500	14,800	2.6

Table 14: Poor batch weight averages and polydispersity Mw/Mn

Good Batch				
Sample	**Run No**	**Mw**	**Mn**	**Polydispersity**
Prefomr				
Weld region root	36	38,400	15,000	2.6
repeat	38	38,500	15,100	2.6
Bottle				
Base fail region	35	39,000	15,300	2.6
repeat	39	39,000	15,300	2.6
Bottle				
base central region	29	39,100	15,300	2.6
repeat	34	39,300	15,400	2.6
Bottle with generic fluid filling				
Fail region	30	38,100	14,900	2.6
repeat	41	38,000	14,900	2.6
Bottle with generic fluid filling				
Base central region	31	37,800	14,800	2.6
repeat	32	37,800	14,800	2.6

Table 15: Good batch weight averages and polydispersity Mw/Mn

3.23 Thickness measurement

TOTAL THICKNESS	Point 1	Point 2	Point 3	Point 4	Point 5
SAMPLE 1	0.434	0.543	0.434	1.882	1.882
SAMPLE 2	0.44	0.437	0.541	1.798	1.798
SAMPLE 3	0.363	0.621	0.543	1.802	1.802
SAMPLE 4	0.361	0.55	0.455	1.765	1.765
SAMPLE 5	0.411	0.565	0.579	1.822	1.822
SAMPLE 6	0.411	0.622	0.541	1.832	1.832
AVERAGE	**0.40**	**0.6**	**0.5**	**1.8**	**1.8**

Table 16: Approximate thickness distribution in various areas of the bottle base.

Chapter 4

Results and Finite Element Analysis

4.1 Finite Element analysis procedure

Finite element analysis was carried out using ANSYS 18.1 to test the different design performance. Objective of the FEA was to model the stress and strain that develops in the bottle base as result of the pressure boundary conditions applied and evaluate bottle base design effect on the ultimate pressure performance of the bottles. Of particular interest was also the location of the critical stresses developed because there are regions in the bottle base (close to the centre) where they can become more critical increasing the chance of bottle burst. Also important was identifying the amount of deformation during the bottle base expansion as it lifts the air connector and the final embodiment will need to cope with the geometrical expansion of the bottle under pressure.

4.2 CAD design

The first step was design the full bottle in full 3D and the core designs were implemented using AUTOCAD engine based packages. The model was first build as a full outer profile and then geometrical 3D cutting tools were applied to the bottle base so to create feet in the base. The simplest profile is the hemispheric that presents no valleys and has a pseudo-spherical outer profile, with this design no cutting tools are needed as the regioned profile is revolved round the Z axis taking advantage of the natural symmetry of the bottle. The final model was exported in DWG format, native format for AUTOCAD engine based packages which was then converted to STEP and IGES formats a common ANSYS model format (we experienced difficulties in important some dwg versions). Note that in the application several forms of air connectors were proposed but not finalised therefore the connector was not modelled also because the central region of the small central bottle base area where the connector seats is the thickest therefore the result are not affected by the absence of the air connector.

The bulk of the stress distribution geometry dependent can be influenced by the channel width (in between feet), number of feet and the curved profile that leads to the central depression where the connector is located and protected. We can therefore evaluate, for example, if it is possible to reduce the higher stress area or move them away from the less stretched areas (in the base centre) more towards the external regions of the bottle base where the PET had the chance to better develop the mechanical properties.

4.3 ANSYS Pre-processing

ANSYS preferred model import for our designs was in STEP format, this proved the most successful overall but IGES is likewise reliable. ANSYS 18.1 includes its own CAD editing tool, SPACECLAIM or Design Modeller. The first is very flexible and powerful that can be used to quickly modify editable CAD designs, de-feature, and extract only FEA relevant assemblies and also to activate parametric analysis that can be useful when progressive geometrical changes are to be evaluated. The STEP imported model was generated and then bottom of the side wall and bottle neck were suppressed as the critical burst area is in the base while the bottle walls are the most stretched and where PET is mechanically stronger. As later shell element will be applied in the mechanical modeller cluster of contiguous areas of the base were selected starting from the outer and moving towards the centre defined four major cluster areas. These will later receive different thicknesses that developed during blowing. The generated face clusters were grouped in a single model part that was imported to ANSYS modeler.

4.4 ANSYS Model Material definition

Before importing the model or at the latest before running the simulations, PET material needs to be created within the ANSYS material library. ANSYS material parameters are entered to capture the overall stress-strain of the material behaviour up to final failure, i.e. the elastic region where the induced stresses are lower than yield strength and material can recover original shape when load is removed, the material plasticity, when the stresses are pushed beyond yielding and the material result in permanent deformations that will not recover when the load is removed. As discussed in the previous chapters PET is one of the materials that when it is strained beyond yielding it undergoes

strain hardening which increases the stress it can support it is therefore important to introduce parameters that define strain hardening behaviour so that non-linear simulations can be performed. ANSYS and other non-linear structural FEA software provide parameters within their libraries that can be set to capture the hardening behaviour of the material therefore getting a more accurate simulation that does not underestimated structure mechanical performance. ANSYS hardening rules, as from ANSYS theory documentation, allow the software to capture how the yield surface changes size, centre, and shape when plastic deformations occur and also to determine when the material will yield again if the load is further applied or is reversed. If the dilation of the material during hardening is considered uniform we can apply isotropic hardening (below picture).

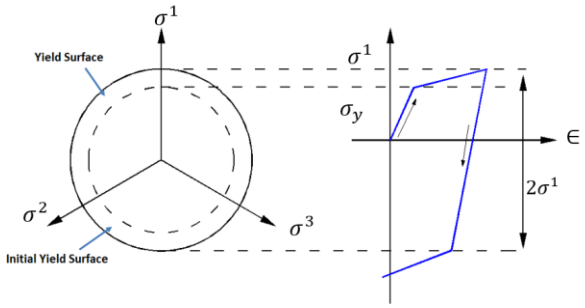


Figure 17: Yield surface

ANSYS allows the user to enter the non-linear parameters by specifying the young modulus and the tangent modulus for bilinear material representation. It is also possible to enter the material as multi-linear by specifying logarithmic strain versus true stresses data points. The bilinear approach is generally perceived as less accurate as in reality there is a different tangent modulus for every strain point above yield (before yield stress strain ration is constant in the elastic region therefore tangent modules is equal to the young modulus) but as the Multi-linear is also more computer demanding it is often acceptable to define the material as bilinear to capture the plastic behaviour, during which shear stress forces cause material planes to slip over one another as the atoms within the crystal structure re-arrange with new neighbours. The materials properties for the PET were defined, isotropic (rather than orthotropic or anisotropic), density (1380 Kg/m^3), Young modulus (3.61E+09 Pa), Poisson ratio (0.4), Bulk modulus (6.017E+09 Pa), Shear modulus (1.2893 E+09 Pa), Bilinear isotropic hardening – Yield strength (9.2E+07 Pa) and Tangent modulus (1000 Pa), Tensile yield strength (9.2E+07 Pa), Compressive yield strength (5E+07), Tensile ultimate strength (9.5E+07).

4.5 ANSYS Analysis setting

Pre-processing setting were defined for the analysis. The Geometry imported was divided in several areas and thicknesses estimating from the likely material typical expansion during blowing together with a plastic bottle blowing expert. Thickness ranged from 0.3 mm at the wall to ca. 1.8 mm at the centre of the base.

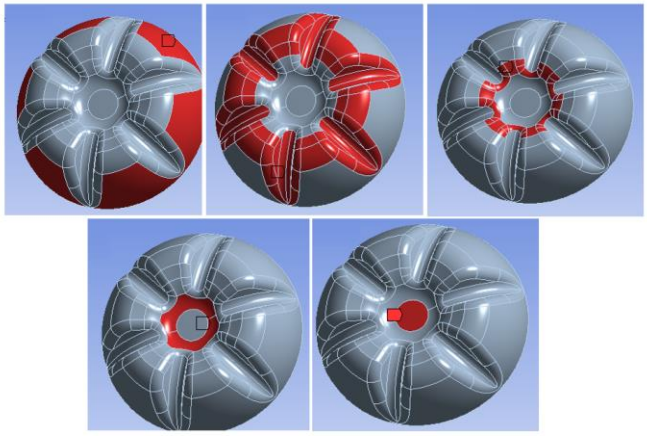


Figure 18: Bottle base thickness areas

Boundary condition, base edges were fixed in x, y, z (space fixed support) while a - 0.2 Mpa pressure (i.e. negative pressure applied from inside towards the outside of the bottle) was applied to the base overall surface with a stepped analysis. To improve convergence the analysis was divided in 3 steps and each steps in further 10 sub-steps (up to 100) so that the pressure was ramped up slowly accordingly. Indeed the initial convergence problems (mostly highly distorted elements that can be more easily identified by looking at the residual forces, adjusting penetration modality, augmented Lagrange was less helpful) were resolved by adopting optimal meshing quality, regionalization thickness, and material plastic properties. Convergence bisection points, i.e. points where ANSYS is forced to divide sub-steps to cope with hard converging solutions were minimal and relegated to the high pressure part of the stimuli curve. From coarse initial simulations it was noted the amount of base deformation is significant therefore, even though it increased computation time, large deflection setting was activated.

4.6 Meshing and convergence

Meshing is the process of dividing the domain into a series of discrete cells so that ANSYS will then solve the equations at the nodes delimiting the unitary cell. Many decades ago FEA meshing of shapes that deviated from regular geometries like cubes and cylinders and their 2D geometry derivatives was extremely difficult but major algorithms improvements during past years can now allow complex design to be meshed, checked and corrected most of the time with reasonable effort. In fact there are now specific software that are dedicated to meshing only and can export meshed model to most FEA programs for particularly difficult geometries.

Good meshing starts from the CAD drawing that is either imported or designed within ANSYS. Right level of featuring is critical in the sense that excessive simplification of the real model will dilute the accuracy while eliminating non necessary features will simplify meshing, reduce computational effort and produce better analysis. Perfect corners, for example should be avoided as they lead to infinite stress that can either fail to converge or generate unrealistically high results.

The bottle models in these studies were cut at the base level in ANSYS retaining only part of the wall as PET is highly stretched in the wall and the rest of the bottle and therefore known to be mechanically capable of coping with these level of pressure. The pressure is to be applied at the centre of the bottle with a connector that is raised over the bottle base and then secured after the preform has been blown. This area of ca. 10 mm is very small and concentrated in an area that is very thick and not expected to flex and as it will only add material it should not impact on the mechanical performance therefore was not modelled. To allow more realistic simulation the bottle base was divided in areas and estimated thickness assigned as from figure 18 above. Later in the project model will be manufactured for testing and simulation re-run using experimental data therefore validating and improving the accuracy. We also plan to use simulation packages like Polyflow that can model the injection of molten PET in the moulds therefore assisting in the design finalisation.

There a number of tools that can help meshing taking advantage of regularities in the design for example sweep, multi-zone and 2D tools for membranes but as the bottle base geometry is very complex and difficult to ensure seamless mesh across the different regions the best approach was to mesh directly on the curve optimising main parameters that control shape and dimension of the cells. Good meshing helps main convergence, has the right density to capture mechanical behaviour

especially in the critical design areas and is therefore made up of sufficient number of nodes and elements and of good quality. Results will stabilize as the mesh density and quality grows till it will reach an equilibrium between computational time and complexity of the model. Choosing the right element associated with the nodes is also important as some elements can increase accuracy and reduce computational time. Within ANSYS once the MESH is selected in the main tree it is possible to visualize the elements and their quality directly on the cad representation window. Aspect ratio, the ration longest to shorted dimension should be closer to 1 (same for the overall Element quality parameter) over the various elements and attempts should be made to improve if lower end of distribution is too close to 0. In version 18, for example, it is possible to select aggressive mechanical (under shape checking option) and the software will attempt to improve automatically the various quality parameters selected. Jacobian ratio is another important parameter. This is a number that is related to the determinant of the Jacobian matrix at various points of all elements (nodes and integration points). Good meshes will have a lower high level of Jacobian ratio and non-negative on the lower scale. Similarly one should optimize the other parameters like for example warping factor, skewness and orthogonal quality. While Workbench version of ANSYS has simplified iteration with the user by uncluttering and trying to automate some of the core functions, on the other hand it has made less obvious to interrogate the system on the many parameters that are important to ensure a robust simulation. For example checking which element type is in use or requesting a specific element type switch requires the introduction of a mechanical command with correct syntax. The bottles were simulated using element type 18.1. For this type of problem this shell element is appropriate and among the most efficient as it is good alternative to solid elements as most of these increase computation time and when resolving thin shells can be affected by issues like transverse shear locking, though this can be managed with adequate refined meshing (SOLID185, SOLID186 20 nodes hex, SOLSHE190 8 nodes solid shell etc.) but uniform meshing is important as if it is not achieved the chances of difficult solution convergence will also increase. For other complex shell geometries extracting adequate mid surface representation might be difficult but again for very low ratio thickness to width shell approach is preferable in spite the aggravation to produce a good geometry. Shell181 is a four node model with 6 DOF per node which allows to model translations and rotations in the x, y, z, directions and is suited for large strain non-linear applications (uniform reduced integration for default which is acceptable provided that the model thickness is discretized in a reasonable amount of

elements, KEYOPT(3) parameter can be set accordingly). Parameter KEYOPT (5), (set to 1) allows simulation to gain in accuracy by taking into account initial curvature effects. Von Mises isotropic hardening plasticity models can be used with material with BISO (bilinear isotropic hardening) and MISO (Multi-linear isotropic hardening) to operate the simulation in the non-linear region. The effects pressure load stiffness are also included with element 181. For designs ready for finalisation a robust convergence study is very important and both element size vs. best mesh statistics should be achieved to guarantee stable solution. This exploratory proposal work is bound to be subjected to further modifications therefore a high accuracy is not needed, nevertheless a basic convergence study was carried out to observe model behaviour and set references for future refinements. We can see max stress tends to project towards 110 MPa in the base region close to the power connector.

Model mesh element size was reduce from 5 mm to 0.5 mm and a central bottle base node away from discontinuity was monitored for Von Mises Stress indicating that for element size smaller than 1 mm it's converged enough for this application.

4.7 Modelling Results

4.7.1 Foot base bottle thickness reference

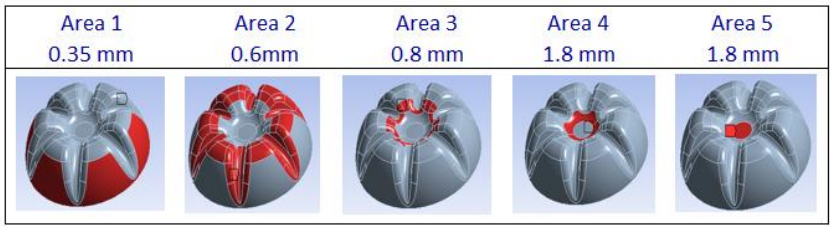


Figure 19: Bottle base Areas 1 to 5 thickness

4.7.2 Equivalent Base Stress result at internal pressure of 2.0 Bar

In picture 20 a contour plot of the stress distribution and total strain in the critical area of the bottle base when loaded with internal pressure of 2.0 bar; in warmer colours (yellow and red) the stress concentration areas.

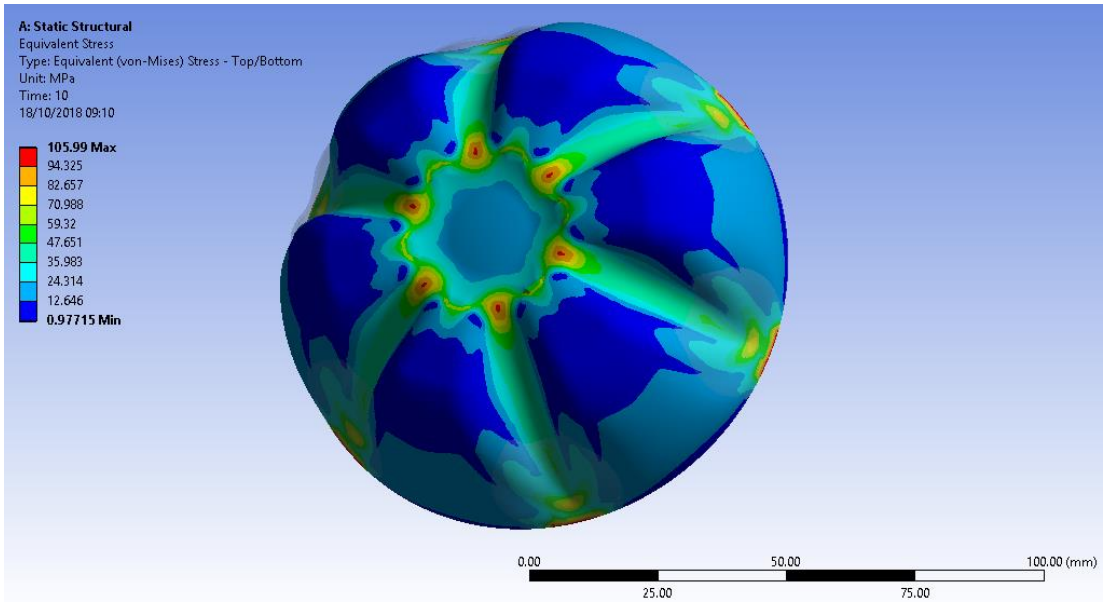


Figure 20: Bottle base Von Mises equivalent stress contour plot at 2.0 bar internal pressure loading

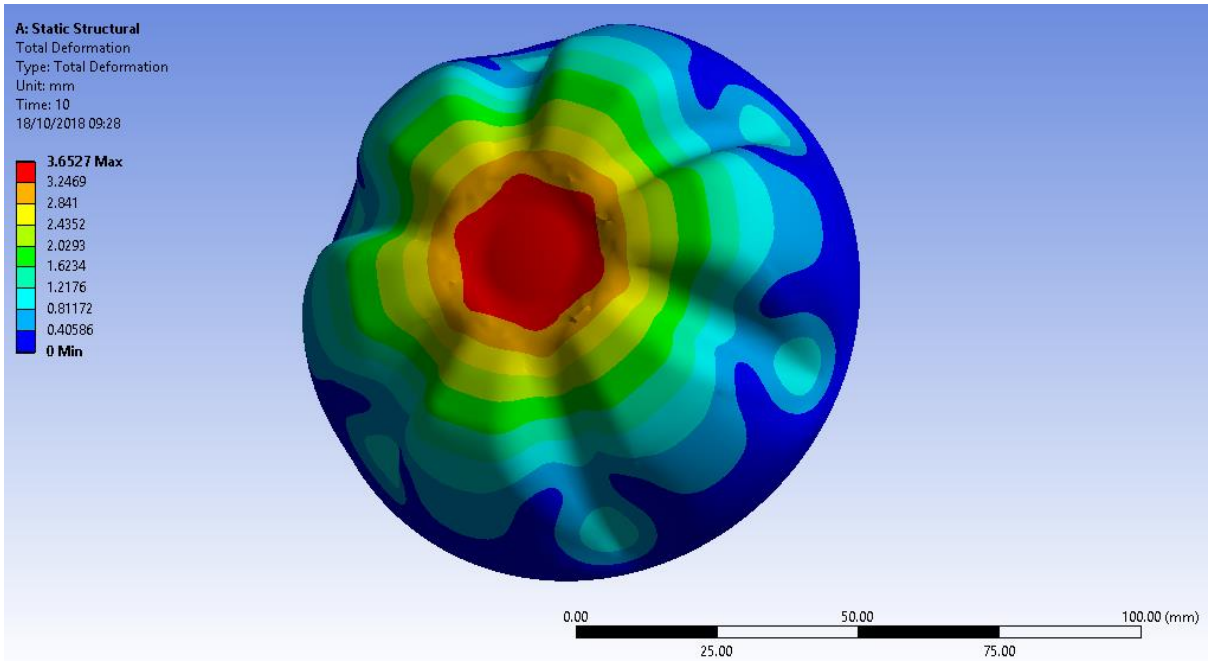


Figure 21: Bottle base Total deformation contour plot at 2.0 bar internal pressure loading

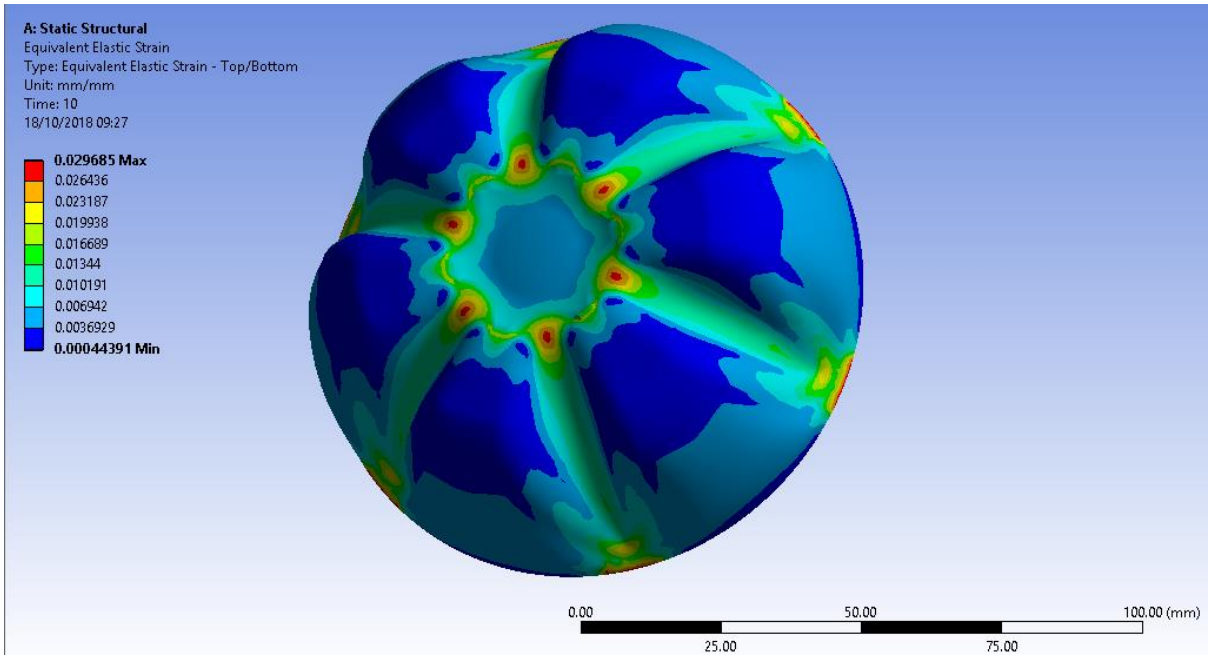


Figure 22: Bottle base strain contour plot at 2.0 bar internal pressure loading

There are in particular two band regions that experience maximum stress at yield stress, one at the base of the bottle in six circular areas right in between feet. These areas raise less concern as PET is highly stretched and orientated in this part of the bottle also the amount of total deformation is low and there is limited curvature complexity therefore burst failure is not expected to originate so far from the bottle base centre. In literature similarly primary failure was found to occur in central part of the base.

The areas of bigger concern are the areas close to centre for different reasons. These areas are in the transitions region where thickness of the PET is likely to increase during blowing. In this region it is also expected a more limited stretching therefore higher chance of failure in addition it will be worst if a pressure port is used here and must be welded in the centre as some form of heat protection will be needed further diminishing the strength the can developed during blowing. The geometry is more convoluted and therefore thicker and keeping the material cooling under control will demand increased effort during production. The centre of the bottle will raise in excess of 3 mm and therefore imperfections must be avoided to ensure bottle maintains integrity during use and cracks can develop. Also if two bottles need to be coupled or attached to secondary structure it will be necessary to allow for such expansion. Another consideration is that since the material yields at the applied pressure some of the material will not be able to return to the initial dimension once the stress is reduced to zero, the base is bound to remain slightly deformed (depending on pressure) after first inflation and

while this shouldn't impact on failure it should be taken into account to ensure coupling is not in interference. The area in red at the centre of the base experiences a similar deformation and therefore should not be impacted by the addition of binding supports for a potential connector port.

4.7.3 Foot base bottle thickness (thicker)

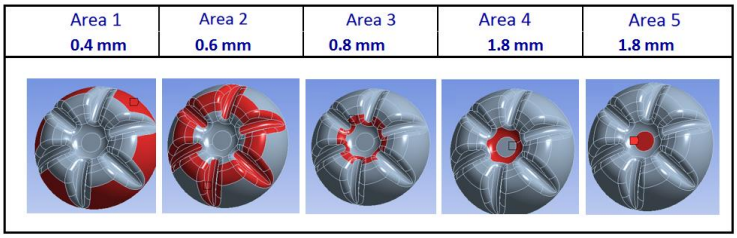


Figure 23: Bottle base Areas 1 to 5 thickness

Equivalent Base Stress result at internal pressure of 2.0 bar picture 25 a contour plot of the stress distribution and total strain in the critical area of the bottle base when loaded with internal pressure of 2.0 bar; in warmer colours (yellow and red) the stress concentration areas.

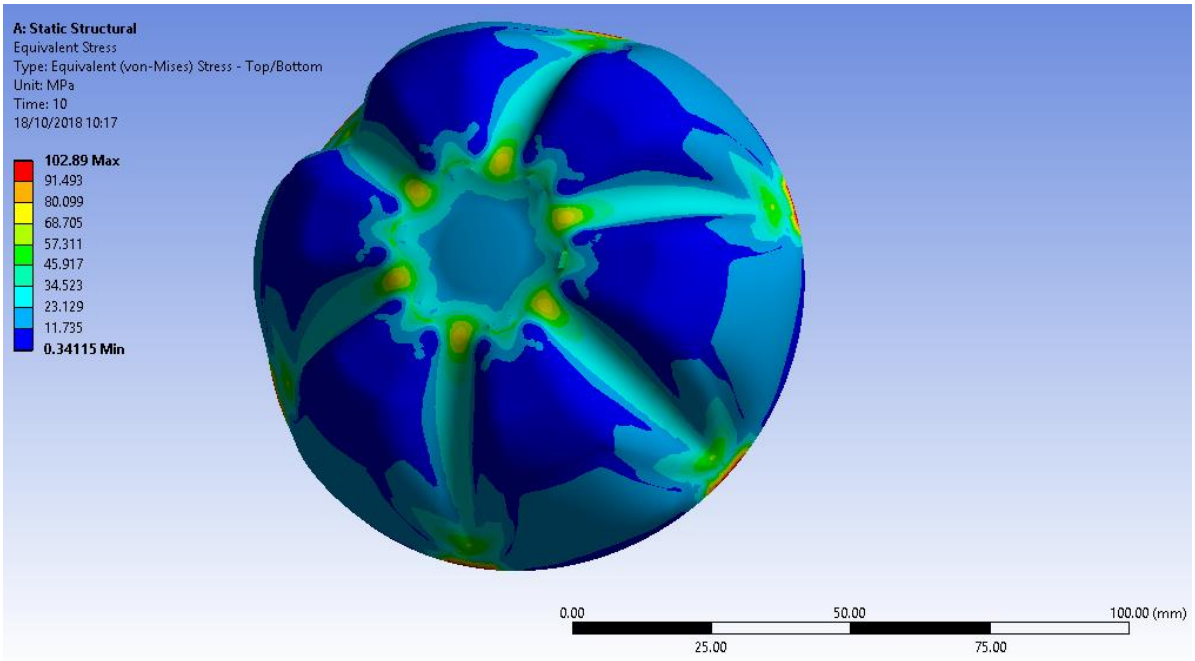


Figure 24: Bottle base Von Mises equivalent stress contour plot at 2.0 bar internal pressure loading

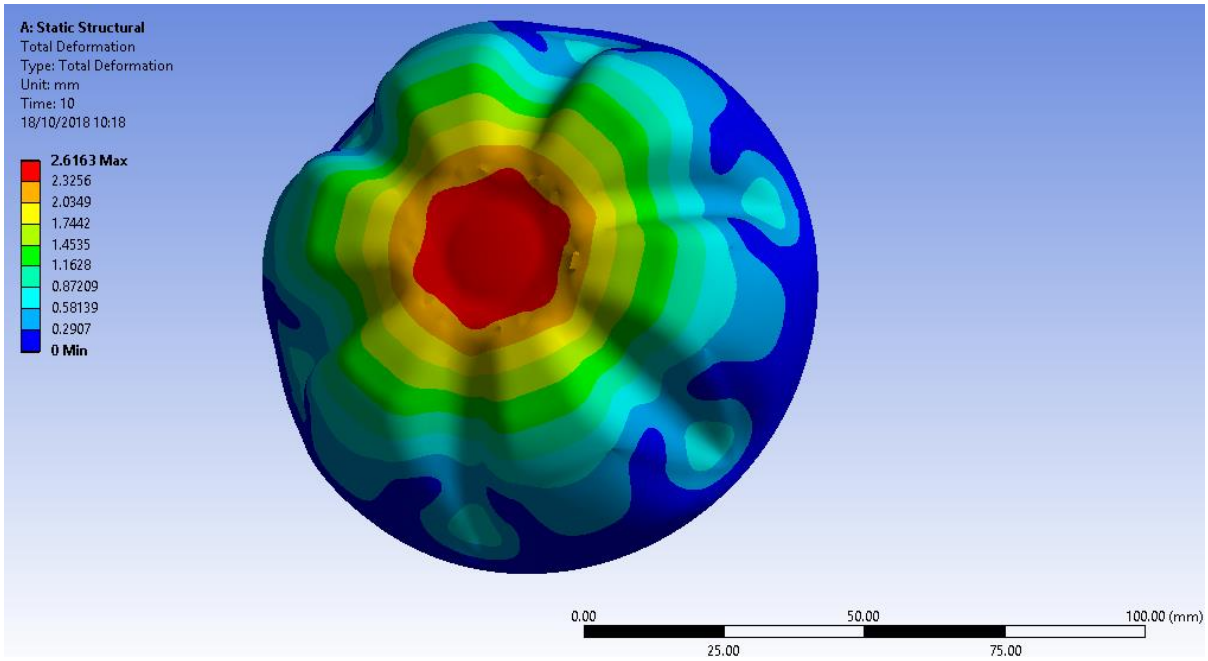


Figure 25: Bottle base Total deformation contour plot at 2.0 bar internal pressure loading

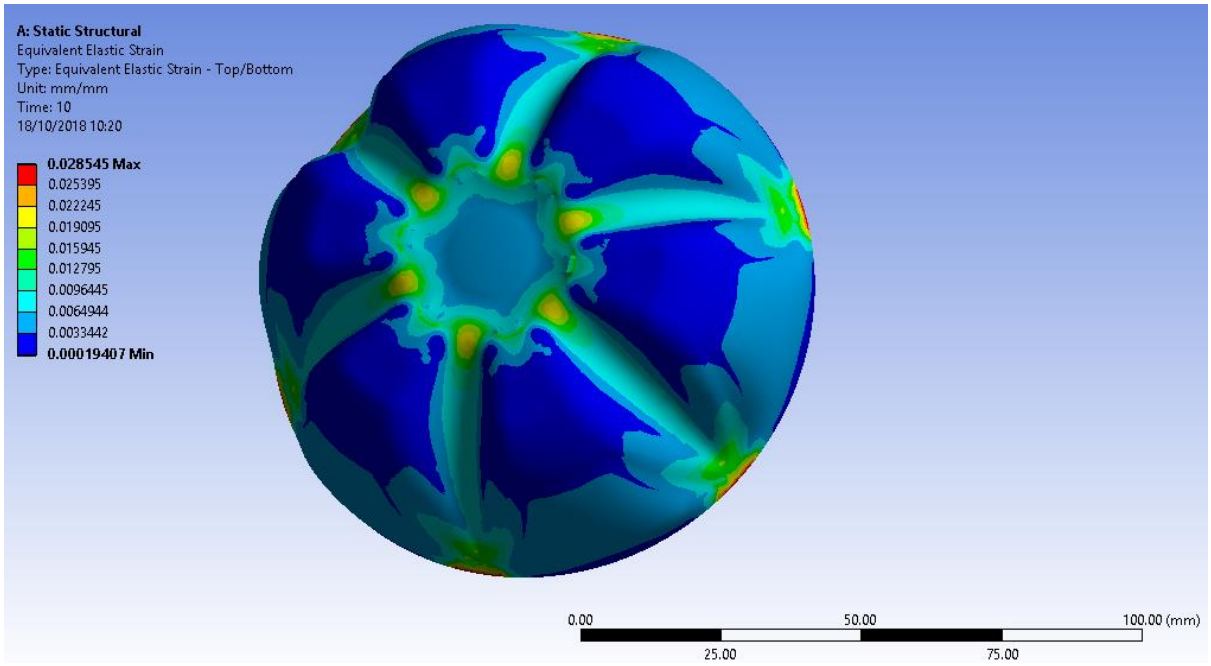


Figure 26: Bottle base strain contour plot at 2.0 bar internal pressure loading

5.0 Discussion and conclusions

- DSC analysis shows that crystallinity degrades towards the center, the area closest to the power connector virtually amorphous. The region of low crystallinity is wider for the burst bottle compared to the standard bottle. In the burst bottle even the outside region is poorly crystalline. The standard bottles outside region is highly crystalline. This confirms that, for this burst bottle, the strengths performance is inferior compared to the standard.

- Bottle bursting: The lower crystallinity for the burst bottle might originate from the blowing process, possibly from excessive rapid cooling of the blown bottle in the mould as this is linked to lower crystallinity, therefore it is recommended to review the cooling stage stage of the blowing machine and assess if process setting and equipment is capable of maintaining appropriate cooling that maximise material crystallinity. It is important to note that cooling should not be too slow as this might induce unorientated polymers to aggregate leading to a spherultic structure which will cause the bottle to look opaque. There are factors that contribute to cristallinity in PET, for example stress induced crystallisation, molecular weight, amount of crystalline phase, degree of molecular orientation, nucleating agents. Note these are pilot productions therefore changes can be expceted during full shift production.
- The failure dynamic observed happens as the pressure is ramped in the bottle, a crack is initiated in the top surface of the outer bottle, in ring area round the central power connector in the base in the transition area thicker less stretched

base with thinner stretched and propagates round the power connector severing it completely from the bottle base. During the fracture progression multiple radial tears shred the rest of the base but this is secondary effect to the initiation crack. The observed failure pressure was below two bar and therefore within the operating pressure of the application and much lower than the maximum pressure the container, correctly manufactured, can withstand which is between ca. 6-7 bar. Poorely produced bottle can fail within first cycle of operations as well as later, within the twenty three nominal operating cycles, fatigue is seen as aggravating factor of the substandard produce but not generally the main cause of failure.

- The fracture analasys does not reveal the presence of defects such as voids, contamination, discontinues within the fractured wall. Some of the failed bottle outers have a cloudy appearance which is normally associated with the blowing thermal history in particular if bottle stretched at higher temperature. A known root cause for PET bottle is environment stress cracking (ESC) where chemical exposure can induce small cracks that can range from visibile to human eye down to microscopical scale (these microscopical cracks can still manifest as haziness and therefore can be recognized). Such cracks can then grow as the pressure is ramped therefore causing such a burst. There is no indication of this phenomena in the tested bottles as well as in the standard bottles.
- GPC analysis showed that, while the original resin demonstrated a slightly higher molecular weight, the bottles and preforms tested share a similar molecular weight result indicating that degradation did not significally occurred in the failing specimen and is therefore not the primary cause of failure.

- DSC study reported in the thermograms show the glass transition temperature (Tg) for the bottle PET material as a small transition between 82°C to 84°C, but the melting point (Tm) ranges from 244° to 248°C suggesting a possible alteration of the PET grade which was reflected in the Tm change. While variable cristallinity levels were observed within the bottle base there was no significant difference between the failing batch and the standard, no significant difference also between the preforms. As the re-crystallization exoterms of the outer bottle show detectable variability it is adviced to exerct a more systematic temperature control during the SBM process. This is particular important in this unusual blow moulding application as the presence of the power connector prevents use of exessive heat in the center base area (that would damage the sealing material on the tip) during blowing therefore increasing the chance of producing poorely thick undestretched material right in the transitional area associated with crack formation which will predispose the failure.
- In normal bottle blowing the preform is injected using a central gate. The precense of the power connector prevents this practise therefore the gate is off center which could affect a clean join of the molten flow opposite to the weld line as the preforms sets in the mould. A weldline is noticable on preforms, bottles and power connector therefore a more systematic flow simulation study is recommended on the mould the evaluate if uneven flow could, in some situations, affect the integrity of the weld line front formation possibly causing a discontinuity in material properties that under heavy strain might favour the formation of a crack deep enough to travel fast causing the burst. It should be

noted though, that a small study of the associated on failed bottles injection gate position to failure region was not strongly associated.

5.1 Geometry considerations

- Many plastic pressurized bottles applications in literature are found within carbonated industry. Pressure within carbonated commercial drink botles is generally constant or it varies slowly over time due to enviromental factors for example temperature and mechanical stress induced by transportation. Cheaper water carbonization which is based a co2 pressurized cylinder exists but bottle is only pressurized during carbonization and then mineral water is poured using gravity feed (several portions).

- Wether constant or ciclic pressure the bottle design and manufacturing process needs to be robust to avoid failure and PET of the correct grade and use is ideal. In this application containment within a mixing outer case is foreseen therefore added safety can be ensured to contain the bottle. A 6 foot bottle design is proposed (to try and contain feet and valleys deformation and strain) and simulated on ansys static structural model. During the pressurization phase the bottle stretches out (this bottle has a 100 mm diameter, if it was wider even more distortion would be expected) and stress develops in various region as result of the compresser air force exerted over the internal bottle surface. Most of the bottle experieces stress values within material yield but there a some regions where the materials is exposed to

stress at ultimate tensile yielding. The first regions (radial regions) occurs at the interface base to bottle main wall and are caused by the base valleys flexing out with the feet.

- While the stress values are high in this regior they are less warrying as PET is highly stretched and is not expected to fail. On the other hand the high stress regions in the central area, close to where the power gate will inject pressurized air, these areas that are at risk of burst for various synergetic reasons. Plastic visco-elastic properties, also function of time, cannot exclude that long exposure to stress can cause failure at lower stress levels than expected. Situation is bound to be more challanging as heat screening of the the central region (if delicate connector is in place before blowing) needs to be monitored and carefully designed as lower heating will furthere reduce PET stretching in this region therefore reducing ultimate strength performance. As this connector needs to protected from dropping impact a flatter bese design is not recommended as any damage to the connector (following a drop for example) will make the bottle useless. A bottle base cover could be used to protect the connector if a flatter base design is to be employed but this will vanify the attempt of reducing environmental impact by saving pastic quantity. On top, if we a base cover (glued) has to be used it is better off employing an hemispheric design which is much more robust, less deformation and less stress in the base). At least looking at smaller diameter should lead to lower deformations (thickness and other parameters kept the same) therefore improving performance.

- Maximum performance should be achieved by looking at all the various aspects of the technology. Design, material choice and handling, manufacturing, process critical control points monitoring and bottle testing (chimical and mechanical).

- Further design refinment is needed. Areas in centre of the bottle base should well within the ultimate stress failure limit but this needs to be considered together with bottle manufacturing as thickness distribution needs also to be considered together with the design. A manufacture trial is needed to evaluate real thickness distribution, while polyflow modelling might help validate the proposed thicknesses a pilot trial is more realistic because of the limited process controll in the blowing technology (for example controlling time and temperature of the different lamps can only reach a compromise between stretching and thickness distribution in the base). Is common misconseption that a general increase of thickness will lead to stronger bottle, especially in this case an excessive increase in thickness could make the bottle weaker. We expect this because the stresses here are very dynamic as the structure is flexed very fast and repetitively and especially if bottle base areas experience even cooling for example, there is a risk that the material layers slide over each other and as the top layer are exposed to high tensile stress the might crack, the crack will travels fast cause the base the explode.

- Another source of cracking could result from the fact that as the centre of the bottle has a hole and a connector therefore the injection gate (where the molten PET is injected in the moulds) can only be placed off center. Rather than having a symmetry

flow round the mould the flow is split in two streams and then join at the opposite side.

- PET material should be of good grade for pressure application that is high enough to be strong but not excessively high that would be difficult to process on the blower. Manufacturer should be able to advice and to recommend right drying temperature and time. This is very important as residual moisture causes poor burst performance.

- Environmental stress cracking agents, like some mould oils need to be avoided at all cost.

- In line pressure testing is recommended. From our simulations we should expect less than 5 mm of deformation. Bottle base should recover most of the original shape after pressurization but experiments are recommended to ensure in line test checks the bottle with minimum alteration of the product.

- Chemical tests should be carried out on the bottles as a reference. DSC in various part of the bottle, especially the centre should give an ideal of the amount of the amorphous material present this can be correlated with burst data and thickness distribution if available.

- Cyclic pressure tests should be carried to check the dynamic performance of the assembly and to ensure no premature (i.e. well within the yield stress of the PET material supplied) occurs.

6.0 Future work

Current FEA evaluation shows that more work is needed to find geometry solution that shift the high stress areas away from the power connector where PET can be becomes fully stretched loosing substantial mechanical performance. While currently power connector is not fully defined having a finalised design could help trying to find ways to keep the base bottle centre hotter and perhaps achieve a better PET structure. The brief investigation of this work appears to suggests that while an optimised design can be achieved amajor part of the final system performance will rely on robust production procedures and ensure all the critical control points and steps. Every bottle should be nominal pressure tested and off line sampling should check maximum burst pressure to monitor the batch (together with all the other tests avaialable relavant to the application). Engaging suppliers, manufacturers and consultants that are qualified and daily deal with pressure challanged bottles is highly recommended.

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